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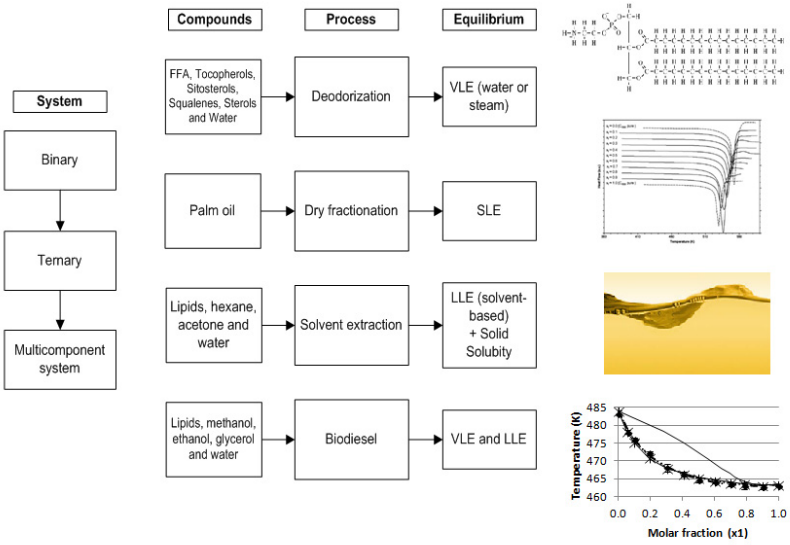

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Ph.D. Thesis
January 2015

DTU Chemical Engineering
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Preface

This thesis is submitted as a partial fulfilment of the requirements for the degree of Doctor of Philosophy (Ph.D.) in Chemical Engineering at the Technical University of Denmark (DTU). This project is a collaboration between the CAPEC-PROCESS center of the Department of Chemical and Biochemical Engineering, DTU, Alfa Laval Copenhagen A/S, Denmark and State University of Campinas (UNICAMP), Brazil. The project has been carried out from February 2012 until January 2015 under the supervision of Assistant Professor Roberta Ceriani, Dr. Bent Sarup and Professor Rafiqul Gani.

I am grateful to my supervisors, Assistant Professor Roberta Ceriani, Dr. Bent Sarup and Professor Rafiqul Gani for their guidance. Special gratitude to Professor Rafiqul Gani for the directions in my project and the opportunities to collaborate with different organizations, which allowed professional and personal growth. Financial support provided from Technical University of Denmark (DTU) and Alfa Laval Copenhagen A/S is also acknowledged.

Special thanks also to Professor J. O'Connell, for the important discussions about this project and academia. The activities in the free time with my colleagues at CAPEC played an important role in my life during the development of this project, adding more colour to the days. My immense gratitude to my family, for their encouragement and love, and to God, for always being present in some way.

Kgs. Lyngby, January 2015 Larissa Peixoto Cunico

“You don't write because you want to
say something; you write because
you've got something to say.”

Scott Fitzgerald

Abstract

Many challenges involving physical and thermodynamic properties in the production of edible oils and biodiesel are observed, such as availability of experimental data and realiable prediction. In the case of lipids, a lack of experimental data for pure components and also for their mixtures in open literature was observed, what makes it necessary to development reliable predictive models from limited data.

One of the first steps of this project was the creation of a database containing properties of mixtures involved in tasks related to process design, simulation, and optimization as well as design of chemicals based products. This database was combined with the existing lipids database of pure component properties. To contribute to the missing data, measurements of isobaric vapour-liquid equilibrium (VLE) data of two binary mixtures at two different pressures were performed using Differential Scanning Calorimetry (DSC) technique.

The relevance of enlarging experimental databank of lipids systems data in order to improve the performance of predictive thermodynamic models was confirmed in this work by analyzing the calculated values of original UNIFAC model and by proposing new interaction parameters for original UNIFAC model and lipids systems. Available thermodynamic consistency tests were applied before performing parameter regressions for well-known thermodynamic models such as NRTL, UNIQUAC and original UNIFAC. The performance of the excess Gibbs energy (G^E) based models was also evaluated for lipids data and the fitted parameters contributed to the extension of the created dababase.

The consistency of the available VLE data has been checked using a general and robust approach developed by the Thermodynamics Research Center (TRC) of the National Institute of Standards and Technology (NIST). For SLE data, consistency tests based on the Gibbs–Duhem equation are not feasible, thus in this project new consistency tests have been developed. Moreover, a methodology that combines solute activity coefficients in the liquid phase at infinite dilution and a theoretically based term to account for the non-ideality in dilute solutions is discussed. The SLE consistency test and data evaluation is performed in a software containing options for data analysis, model analysis and parameter regression.

Resume på dansk

Fysiske og termodynamiske egenskaber af madolier og biodiesel giver anledning til adskillige udfordringer, såsom deres begrænsede tilgængelighed af eksperimentelle data og pålideligheden af estimering af disse. I tilfælde af lipider blev en mangel på eksperimentelle data for rene komponenter samt deres blandinger observeret i den åbne litteratur, hvilket gør det nødvendigt at udvikle pålidelige, prædiktive modeller baseret på den beskedne mængde data til rådighed.

Et af de første skridt i dette projekt var oprettelsen af en database med blandingsegenskaber, der er involveret i opgaver i relation til procesdesign, -simulering og -optimering samt design af kemikaliebaserede produkter. Denne database blev kombineret med en eksisterende database for lipid-renkomponentsegenskaber. For at bidrage til mængden af eksperimentelle data, blev målinger af isobare dampvæskeligevægtsdata (VLE) for to binære blandinger under to forskellige ved brug af Differential Scanning Calorimetry (DSC) teknik.

Relevansen af at udvide den eksperimentelle databank med data for lipidsystemer med henblik på at forbedre ydeevnen af prædiktive termodynamiske modeller blev bekræftet i dette arbejde. Dette blev gjort ved at analysere de beregnede værdier ved brug af Original UNIFAC-model og ved at foreslå nye interaktionsparametre for lipidesystemer i Original UNIFAC-model. Tilgængelige termodynamiske konsistenstests blev anvendt på eksperimentelle datasæt, efterfulgt af udførelse af parameterregressioner for velkendte termodynamiske modeller såsom NRTL, UNIQUAC og Original UNIFAC. Ydeevnen af overskuds Gibbs energi-baserede (G^E) modeller blev ligeledes evalueret på lipiddata, og de dertil tilhørende tilpassede parametre udgør ligeledes et bidrag til databasen.

Konsistensen af de tilgængelige VLE-data er blevet kontrolleret via en generel og robust fremgangsmåde udviklet af Thermodynamics Research Center (TRC) i National Institute of Standards and Technology (NIST). For SLE-data er konsistenstests baseret på Gibbs-Duhem ligningen ikke mulige, så nye konsistenstests er blevet udviklet i dette projekt. Nogle af de udviklede tests er baseret på kvalitetstests for VLE-data samt en metode, der kombinerer det opløste stofs aktivitetskoefficienter i den flydende fase ved uendelig fortynding med et teoretiskbaseret udtryk, der tager højde for ikke-idealitet i fortyndede opløsninger. Disse metoder er ligeledes blevet diskuteret. SLE-konsistenstest og evaluering af data udføres i en software, der muliggør dataanalyse, modelanalyse og parameterregression.

List of symbols

$\underline{\underline{A}}$	molecular interactions parameters in generic form of UNIQUAC model
$\underline{\underline{a}}$	group interaction parameters in generic form of original UNIFAC model
A_{kl}^{CC}	an intermediate variable used to predict the group interaction parameter between the groups k and l
A_i	occurrence of atom of type-i
A_{ij}	molecular interactions parameters in NRTL and UNIQUAC model for molecules i and j
a , b , c	parameters of FST model
a_i	contribution of atom of type-i
a_{kl}	UNIFAC group interaction parameter between group k and group l
b_{X-Y}	0^{th} – order CI-interaction parameter between atom X and atom Y
C_i	contribution of first-order group of type-i
c_{X-Y}	1^{st} – order CI-interaction parameter between atom X and atom Y
D_j	contribution of second-order group of type-j
d_{X-Y}	2^{nd} – order CI-interaction parameter between atom X and atom Y
E_k	contribution of third-order group of type-k
e_{X-Y}	3^{rd} – order CI-interaction parameter between atom X and atom Y
$f(X)$	function for property X
f_2^0 , f_3^0	coefficients related to integrals of infinite-dilution molecular correlation functions
G^E	excess Gibbs energy

G_f	standard Gibbs energy of formation [kJ/mol]
H_f	standard enthalpy of formation [kJ/mol]
H_{fus}	normal enthalpy of fusion [kJ/mol]
$J(\boldsymbol{P}^*)$	local sensitivity of the model to variations in estimated model parameters
M_j	occurrence of second-order group of type-*j*
MW	molecular weight of pure component
N	number of experimental data-points used in the regression
N_i	occurrence of first-order group of type-*i*
N_c	total number of carbon atoms in the molecule
N_{cs}	number of carbons of the alcoholic part in fatty esters
N_k	number of groups *k* in the molecule
$n_X^{(k)}$	number of atoms of type X in the group k
O_k	occurrence of third-order group of type-*k*
P_c	critical pressure [KPa]
P^{sat}	Saturated pressure [KPa]
$\underline{Q}_k$	group the surface area parameters in generic form of original UNIFAC model
$Q_{test,i}$	quality factor for each thermodynamic consistency test *i*
$\underline{q}$	surface area parameters in generic form of UNIQUAC model
R	ideal gas constant
R^2	coefficient of determination
$\underline{R}_k$	group van der Waals volumes parameters in generic form of original UNIFAC model

$\underline{r}$	molecular van der Waals volume parameters in generic form of UNIQUAC model
T_b	normal boiling point [K]
T_c	critical temperature [K]
t_i^0	pure melting point temperature of the compound *i*
T	system temperature
T_m	normal melting point [K]
$t(v, \alpha_t/2)$	t-distribution value corresponding to the $\alpha_t/2$ percentile
V_c	critical volume [cc/mol]
V_m	liquid molar volume at 298 K [cc/kmol]
X^{exp}	experimental property value
X^{pred}	predicted property value
x_i	liquid molar fraction for compound *i*
y_i	Vapour molar fraction for compound *i*

Greek symbols

$\underline{\alpha}$	parameters in the generic form of NRTL model
γ_i	activity coefficient for compound *i*
γ_1^∞	infinite dilution activity coefficient
γ_1^*	unsymmetric convention activity coefficient
π	mathematic constant (Pi number)
θ_1, θ_2	uncertainty for the melting point considered in the quality factor equation
σ_i	estimated standard deviation of measurement uncertainty

$\underline{\boldsymbol{\tau}}$	parameters that are functions of the molecular interactions in the generic form of NRTL model
${}^{v}\chi^{0}$	zeroth-order (atom) connectivity index
${}^{v}\chi^{1}$	first-order (bond) connectivity index
ν	degrees of freedom

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Chapter 1. Introduction

The availability and reliability of properties of pure components and their mixtures play an important role in process and/or product design. There are three ways in which a property user can obtain the data for the needed properties: (i) by retrieving the property information available in databases/open literature; (ii) by performing laboratory measurements for the needed properties; and/or (iii) by employing suitable property prediction methods. A key limitation associated with the use of databases is the limited number of chemicals (and sometimes limited number of properties) stored in the database. Chemical and process industries that use computer-aided tools (for example, process simulators such as PRO/II®, ASPEN® etc.) rely on the availability of data and models for properties listed in their built-in databases. Therefore, a lack of necessary physical and thermodynamic properties in the databases restricts the use of computer-aided tools for synthesis-design and modeling-simulation of chemical processes. While the use of experimentally measured property values is highly desirable, laboratory measurements may be time consuming, expensive, and sometimes may not even be feasible. Therefore, it is more practical and convenient to employ property prediction methods in order to obtain the needed property information, at least in the early stages of process and/or product design.

Property prediction methods can be classified into methods for predicting primary properties of pure components (such as normal boiling point, critical constants, normal melting point etc.), methods for predicting temperature dependent properties of pure components (such as vapour pressure, heat capacity, viscosity etc.), and methods for predicting properties of mixtures (vapour-liquid equilibria (VLE), liquid-liquid equilibria (LLE), and solid-liquid equilibria (SLE)). Several types of property prediction methods, such as group-contribution (GC), quantitative structure-property relationship (QSPR), equations of state (EoS), and molecular modelling are available for the prediction of necessary properties. Among these methods, the GC based property prediction methods are widely used in process and/or product design since these methods are fast, efficient, and do not require substantial computational efforts. Although applications of GC methods (for pure components and for their mixtures) in chemical and petrochemical industries are well-known, this is not the case for the lipid processing industry. Commercial process simulators usually lack the availability of

necessary physical and thermodynamic property data and/or models for many of the lipids in their databases thus limiting the wide application of computer-aided methods and tools for process synthesis, modelling and simulation within this industry. The costs associated with separation processes are often a very large portion of the total cost of a whole lipids processing plant, hence accurate and reliable predictions of phase equilibria become important. Moreover, the work of a property model developer is becoming more challenging due to the requirements of prediction of properties of new and complex lipid compounds and their mixtures for which no data are available in the databases / literature. All these issues justify the effort made for developing models for the prediction of properties of lipid compounds and their mixtures and for implementing them to achieve reduced time and cost of the design of better lipid products and processes.

1.1 Thesis organization

This thesis is organized in chapters. In this first chapter – Introduction – the importance of consistent physical and thermodynamic properties for process design, simulation, and optimization is discussed. Chapter 2 – Theoretical Background – presents the available work in the literature related to this project. Chapter 3 – Database – describes the extension of the existing knowledge during the duration of this project, starting with the extension of the pure component database with the information of mixture properties. Chapter 4 – Property model analysis – brings the analysis of thermodynamic models performance for lipids system, with focus in group contribution methods, such as the extension of the original UNIFAC model. Chapter 5 – Thermodynamic consistency test – describes the utilized consistency tests for VLE data and the development of the new thermodynamic consistency tests for SLE. Chapter 6 – Iodine value and cloud point estimation for lipids – brings the developed method for estimation of iodine value and clould point utilizing the information of compounds composition in vegetable oils and biodiesel. Chapter 7 – Experimental work procedure – presents the obtained results together with the highlight of the important features of the VLE measurements. Finally, Chapter 8 – Conclusions and Future work – presents some of the conclusions of this project and give some perspectives for future work.

Additional information is given in Appendices 1-5. Appendix 1 contains information available in the database, which includes phase equilibria properties for binary and

multicomponent systems. Appendix 2 gives a full list of fitted model parameters tables for well-known thermodynamic models such as NRTL, UNIQUAC and original UNIFAC. In Appendix 3, MoT codes created for parameter regression considering the thermodynamic models (NRTL, UNIQUAC and original UNIFAC), and the different objective functions considered for lipids systems to represent VLE, SLE and LLE data are given. It also includes the Fluctuation Solution Theory (FST) model for SLE. The list of the estimated quality factors obtained from the thermodynamic consistency tests are given in Appendix 4. In Appendix 5, the list of the conference participations and publications related to this project is presented.

Chapter 2. Theoretical background

This chapter starts with an overview of the relationship between the phase equilibria and related properties, followed by the definition of lipids and their classification, in addition to statistics related to production and consuption of vegetable oils and biodiesel. Moreover, the current state-of-art for modelling of mixture properties is described with focus on group contribution methods. It is known that consistent thermodynamic model parameters may not be obtained if the experimental data used contain high levels of uncertainties. Therefore, in this chapter, an overview of available thermodynamic consistency tests is given. Finally, the theoretical background of the laboratory measurements for VLE related to this work is presented.

2.1 Introduction

Under mixture properties, in this project the phase equilibria related properties- that is, VLE, SLE and LLE have been considered. For parameter regression of properties related to phase equilibria using G^E based models, it is necessary to: (i) develop a database containing experimentally measured values of properties of pure components as well as their mixtures; (ii) analyze and assess the quality of the experimental data using thermodynamic consistency tests; and (iii) establish a systematic approach for performing parameter regression, including the selection of the most appropriate objective function for the parameter regression.

The experimental data necessary for the modelling of properties related to phase equilibria are discussed together with thermodynamic consistency tests that are necessary for the verification and assessment of the quality of the phase equilibria data-sets. The workflow for modelling various mixture properties using property prediction methods (such as, UNIQUAC, original UNIFAC, and NRTL) is illustrated in Figure 1. After evaluation of the perfomarce of G^E based model, focus was giving in predictive thermodynamic models based on group-contribution.

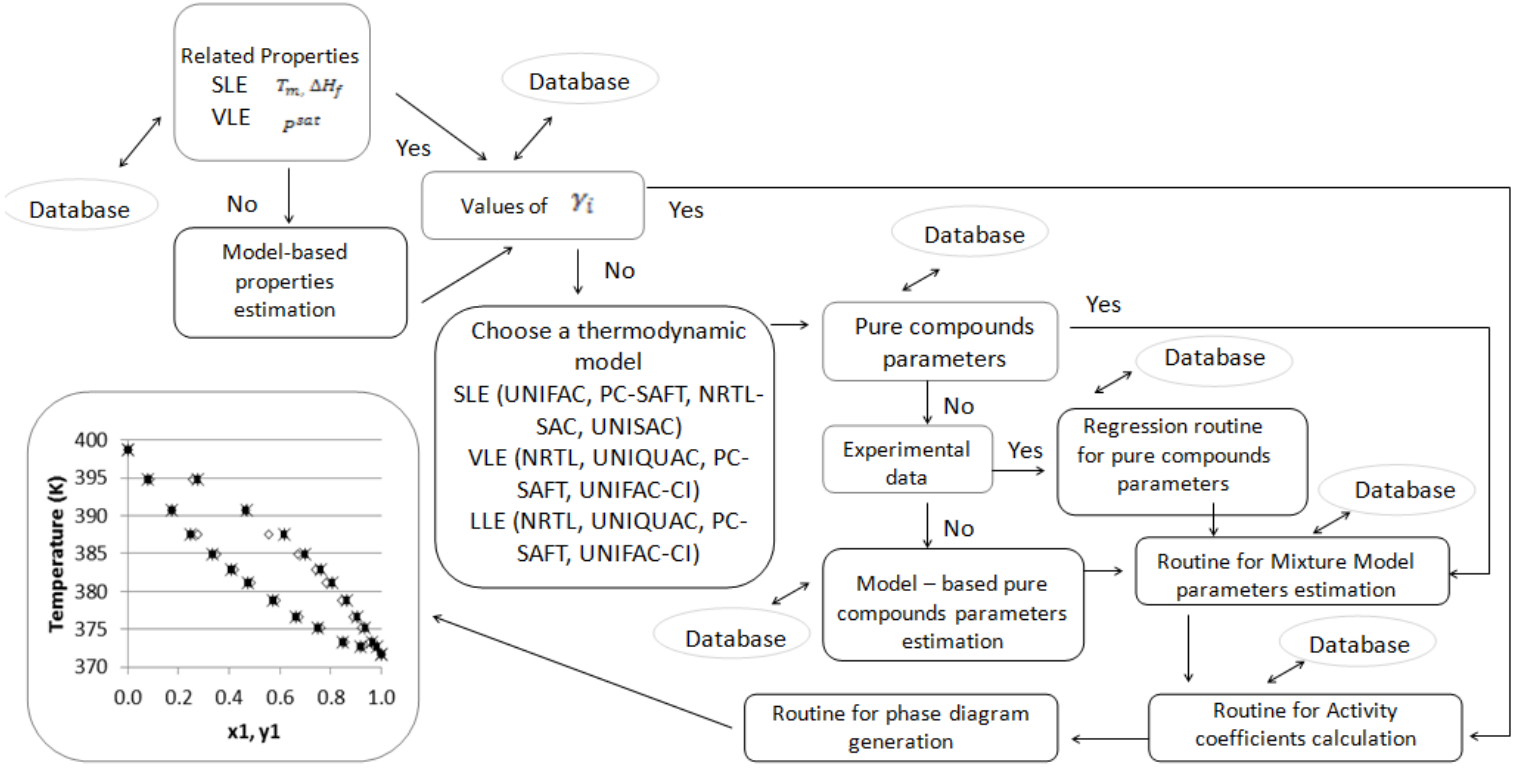

Figure 1: The necessary work-flow/data-flow for SLE, VLE and LLE.

2.2 Current state-of-the-art

In this part of Chapter 2, the achievements in the field of modelling of phase equilibria and related properties reported in open literature are revised together with a description of concepts employed in this project.

2.2.1 Lipids and the world scenario of vegetable oils

Lipids constitute a group of naturally occurring molecules that include fats, waxes, sterols, fat-soluble vitamins (such as vitamins A, D, E, and K), monoacylglycerols, diacyglycerols, triacylglycerols, phospholipids, and others [1]. Lipids have a substantial portion of aliphatic or aromatic hydrocarbon part and other functional structures such as acids, esters or alcohols, as can be seen in Figure 2:

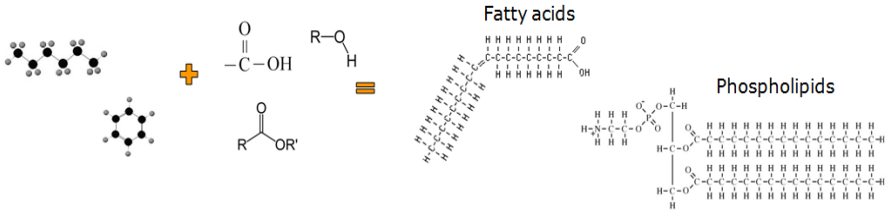

Figure 2: Aliphatic or aromatic hydrocarbon part plus a functional structure for lipids examples.

Lipids are organic compounds insoluble in polar solvents (such water), and soluble in organic solvents (such as chloroform and acetone) and alcohol. They are molecules that are totally or in part originate from carbanion-based condensations of thioesters, as fatty acids, and/or originate by carbocation-based condensations of isoprene units, as sterols [2]. The classification of lipids is shown in Figure 3. In this work, the main classes of lipids present in edible oils and biodiesel production systems, such as fatty acids, esters (methyl and ethyl), triacylglycerols (TAGS), diacylglycerols (DAGS), monocylglycerols (MAGS), phospholipids, tocopherols, squalenes, among others, are considered.

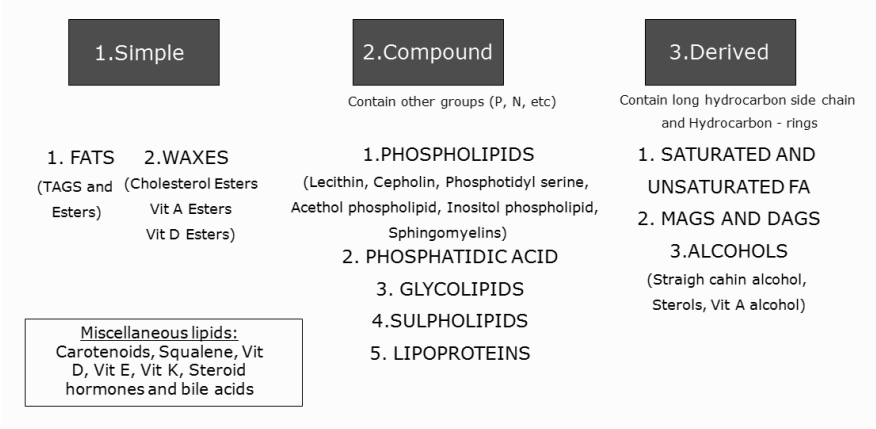

Figure 3: Simplified classification of lipids.

The world's production of oils and fats has grown from 79.2 million tons in 1990 to nearly 176 million tons in the year 2011 [3]. The use of vegetable oils in biodiesel production continue to grow, as indicated in studies from 2000 to 2013 [4]. Such a growth in the production of oils and fats together with consumer's increasing preference for better quality products offer major challenges to lipid processing industry in terms of design and development of better products and processes. Aiming a comparison between different types of vegetable oils, the global production and consumption (million metric tons) and prices (U.S. Dollars per metric tons) can be seen in Figure 4. One of the major reasons for the usage of palm oil (see Figure 4) is that it provides a higher quantity of vegetable oil per unit area of land than any other commercial oil crop. The triacylglycerol composition (around 95% in vegetable oils) in palm oil is mainly due to unsaturated acids (>58,25% oleic acid and >18,41% linoleic acid) [5].

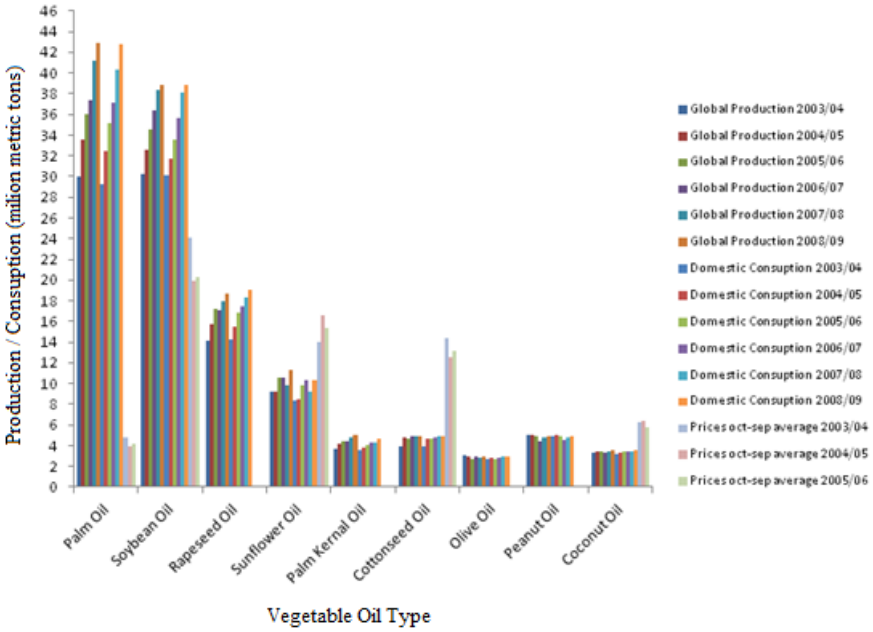

Figure 4: Global production (million metric tons) and global domestic consumption (million metric tons) for different types of vegetable oils, and prices (U.S. Dollars per metric ton). Source of the data [6].

2.2.1 Modelling of mixture properties

For the estimation of bulk-mixture properties such as density, viscosity, surface tension of lipids systems, several GC methods have been reported in the literature. For example, Rabelo et al. [7] developed a model to predict the liquid viscosities of mixtures of fatty acids; Eiteman and Goodrum [8] developed a model to estimate the densities and viscosities of low molecular weight mixture of triacylglycerols.

The prediction of phase equilibria related mixtures properties of lipids based on G^E models such as NRTL, UNIQUAC and original UNIFAC has been discussed by Coelho et al. [9]. Carmo et al. [10] have analyzed different thermodynamic models (NRTL, UNIQUAC, original UNIFAC, ASOG [11], UNIFAC-LLE [12] and UNIFAC-Dortmund [13]) in the representation of LLE ternary systems containing biodiesel and have found that UNIFAC-Dortmund model gives the best experimental data representation. Kanda et al. [14] have considered the same thermodynamic models with exception of ASOG model [11] to describe LLE ternary systems also containing fatty

esters and observed that the best experimental data representation was obtained correlated models such as NRTL and UNIQUAC.

The fact that the intermolecular forces cause non-random arrangement of molecules in the mixture, the arrangement of molecules and their preferred orientation in equilibrium at the interphase are considered in G^E calculation:

$$\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i \text{, for } i = 1, \text{NC} \tag{1}$$

The most well-known molecular models for the calculation of the activity coefficient, such as NRTL, and UNIQUAC, and the predictive GC based original UNIFAC models are discussed below. For each case, the generic form of the equation is shown, that is, the activity coefficient is expressed as a function of specified (or known) variables.

NonRandom Two Liquid (NRTL)

For each binary pair of compounds, the generic form of the NRTL [15] equation is given as:

$$ln\gamma_i\big|_{NRTL} = f\left(\underline{x}, T, \underline{\boldsymbol{\tau}}, \underline{\alpha}\right), \text{ for } i = 1, \text{NC} \tag{2}$$

Where $\underline{x}$ are the molar fractions of each compound, T is the temperature of the system, the parameters $\underline{\boldsymbol{\tau}}$ are functions of the molecular interactions whose values are obtained through regression of the measured data, and $\underline{\alpha}$ are the parameters that consider the constant characteristic of the non-randomness of the mixture.

UNIversal QUAsi-Chemical (UNIQUAC)

For each binary pair of compounds, the generic form of UNIQUAC [16] equation is given as:

$$ln\gamma_i\big|_{UNIQUAC} = f\left(\underline{x}, T, \underline{\boldsymbol{A}}, \underline{r}, \underline{q}\right), \text{ for } i = 1, \text{NC} \tag{3}$$

Where $\underline{x}$ are the molar fractions of each compound, T is the temperature of the system, the parameters $\underline{\boldsymbol{A}}$ are molecular interactions whose values are obtained by regression of the measured data and $\underline{r}$ and $\underline{q}$ are measures of molecular van der Waals volume and surface area of each compound.

2.2.2.1 Predictive thermodynamic models

For mixtures, a GC method that is widely used for prediction of phase equilibria is the UNIversal Functional Activity Coefficient (UNIFAC) model. Further revisions and extensions of the original UNIFAC, as well as the modifications to original UNIFAC (modified-UNIFAC, Dortmund, modified-UNIFAC, Lyngby, and KT-UNIFAC) have been made for taking into account for various limitations. One of the main drawbacks of the UNIFAC models is the need for group-interaction parameters (nearly 50% of the parameters are missing in the parameter table). Revisions of UNIFAC parameters have been done many times in the past but there are still missing entries in the UNIFAC parameter table due to the lack of measured data. This restricts the use of UNIFAC models for predicting phase equilibria for a wider range of chemical systems. To overcome this limitation, a method based on GC^{+} approach (UNIFAC-CI method) is developed to generate the missing UNIFAC group-interaction parameters without the need for new measured data and using only the structural information of the groups [18]. This is achieved by expressing the UNIFAC group-interaction parameters as a function of molecular descriptors with the stoichiometry of the atoms playing a role in the calculation. The development and application of UNIFAC-CI method to predict the VLE and SLE for different systems is reported by González et al. [18] and Mustaffa et al. [19]. The generic form of the equation is shown for UNIFAC-CI. Also, Teles dos Santos et al. [20,21] discussed the application of SLE modelling to predict the Solid Fat Content (SFC) versus temperature.

Original and modified UNIFAC model extended to lipids systems were previously reported in literature, as in Belting et al. [22] work, where UNIFAC model representation was improved in the calculation of infinite dilution activity coefficient in systems containing triacylglycerols (TAGS) and solvents, such as ethanol, methanol and n-hexane. Such improvement was observed by reducing the frequency of ester groups. For LLE, Hirata et al. [23] used a lipids database to regress parameters for original UNIFAC and includes two new groups for TAGS. Validation methods for new sets of group contribution parameters proposed for thermodynamic models are normally not observed in the literature for GC methods. Cross-validation was considered in for COSMO-RS method in the prediction of aqueous solubility of drugs and pesticides by Klamt et al. [24]. In other work, Liang and Gallagher [25] used cross-validation method for Quantitative Structure Property Relationships (QSPRs) to predict physical and chemical properties.

To illustrate how group contribution only utilize the structure of the molecule to predict properties, such for original UNIFAC model, an example a lipid was selected and can be seen in Figure 5.

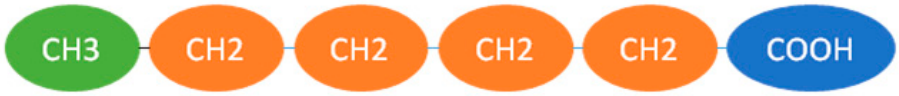

Figure 5: Illustration of group contribution and hexanoic acid for original UNIFAC model.

UNIversal quasi-chemical Functional group Activity Coefficients (UNIFAC)

The generic form of the GC based UNIFAC [17] method is written as:

$$ln\gamma_i\big|_{UNIFAC} = f\left(\underline{x},\ T,\ \underline{\boldsymbol{a}},\ \underline{R},\ \underline{Q}\right), \text{ for } i = 1, \text{NC} \tag{4}$$

Where $\underline{x}$ are the molar fractions of the each compound, T is the temperature of the system, $\underline{\boldsymbol{a}}$ are the group interaction parameters obtained through regression of the measured data, $\underline{R}_k$ and $\underline{Q}_k$ are the group van der Waals volumes and group surface area, respectively.

Group Contribution (GC)-Atom Connectivity Index (CI) approach (UNIFAC-CI)

Atom connectivity indices can also represent the groups used in the UNIFAC model and the regressed atom connectivity index (CI) -interaction parameters can be used to predict the missing group-interaction parameters [18,19]. For the application of the UNIFAC-CI approach, the atom interaction parameters (AIP), a, b, c and d are used to predict the missing group interaction parameters (GIP), a_{kl}, using following Eqs. (6)-(10) as given by Gonzáles et al. [18].

$$\begin{aligned}
a_{kl} &= \underbrace{b_{C-C}\left(A_{kl}^{CC}\right) + b_{C-O}\left(A_{kl}^{CO}\right) + b_{C-N}\left(A_{kl}^{CN}\right) + \ldots}_{for\ 0\ order\ interactions} \\
&+ \underbrace{c_{C-C}\left(A_{kl}^{CC}\right) + c_{C-O}\left(A_{kl}^{CO}\right) + c_{C-N}\left(A_{kl}^{CN}\right) + \ldots}_{for\ 1st\ order\ interactions} \\
&+ \underbrace{d_{C-C}\left(A_{kl}^{CC}\right) + d_{C-O}\left(A_{kl}^{CO}\right) + d_{C-N}\left(A_{kl}^{CN}\right) + \ldots}_{for\ 2st\ order\ interactions} \\
&+ \underbrace{e_{C-C}\left(A_{kl}^{CC}\right) + e_{C-O}\left(A_{kl}^{CO}\right) + e_{C-N}\left(A_{kl}^{CN}\right) + \ldots}_{for\ 3th\ order\ interactions}
\end{aligned} \tag{5}$$

With,

$$\left(A_{kl}^{XY}\right)_0 = \frac{n_X^{(k)}\,{}^{v}X^{0}{}_{(l)} - n_Y^{(l)}\,{}^{v}X^{0}{}_{(k)}}{{}^{v}X^{0}{}_{(l)}\,{}^{v}X^{0}{}_{(k)}} \tag{6}$$

$$\left(A_{kl}^{XY}\right)_1 = \frac{n_X^{(k)}\,{}^{v}X^{1}{}_{(l)} - n_Y^{(l)}\,{}^{v}X^{0}{}_{(k)}}{{}^{v}X^{1}{}_{(l)}\,{}^{v}X^{0}{}_{(k)}} \tag{7}$$

$$\left(A_{kl}^{XY}\right)_2 = \frac{n_X^{(k)}\,{}^{v}X^{1}{}_{(l)} - n_Y^{(l)}\,{}^{v}X^{1}{}_{(k)}}{{}^{v}X^{1}{}_{(l)}\,{}^{v}X^{1}{}_{(k)}} \tag{8}$$

$$\left(A_{kl}^{XY}\right)_1 = \frac{n_X^{(k)}\,{}^{v}X^{2}{}_{(l)} - n_Y^{(l)}\,{}^{v}X^{0}{}_{(k)}}{{}^{v}X^{2}{}_{(l)}\,{}^{v}X^{0}{}_{(k)}} \tag{9}$$

Where $n_X^{(k)}$ is the number of atoms of type X in the group k, ${}^{v}X^{m}{}_{(k)}$ is the m^{th} order valence connectivity index for the group k, A_{kl}^{CC} is an intermediate variable used to predict the group interaction parameter a_{kl} between the groups k and l, and the regressed coefficients *a*, *b*, *c*, *d* and *e*, represent the atomic interactions between the C, H, O, N, and Cl atoms.

2.2.2.2 Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) combined with GC methods

Since the work of Van der Waals [26] in 1873, equations of states (EoS) have been extensively utilized to describe phase equilibria in chemical and related industries due to their applicability in a large range of temperature and pressure. For mixtures at high pressure, equations of state such as Soave-Redlich-Kong (SRK) [27] and Peng-Robinson (PR) [28] generally shows good results [29–34]. However, for low pressure and strong non-ideal mixtures, activity coefficient models such as NRTL [15], UNIQUAC [16] and UNIFAC [17] have shown better representation of the liquid phase non-ideality [35]. Mixing rules that combine excess G^E and EoS models have been proposed aiming to improve the EoS model representation of the non-ideal liquid phase, such as Huron and Vidal [36], Michelsen [37] and Wong and Sander [38].

Considering the industrial use of thermodynamic models, it would be desirable a tool that can calculate the entire phase diagram, including VLE, vapour-liquid-liquid equilibrium (VLLE), LLE and SLE. Also for the cases where the vapour phase is also

non-ideal in VLE systems, it would be preferable if both phases (liquid and vapour) could be described using the same thermodynamic model.

In view of the limitations observed in the use of existing EoS, the so called "next generation" of EoS, Statistical Associating Fluid Theory (SAFT) [39–42] appeared in the 1990s to modify the scenario of the equations of state. SAFT EoS and its modifications, such as PC-SAFT [43,44], LJ-SAFT [45–51], VR-SAFT [52] and simplified-PC-SAFT [53,54], among others, have been used for physical and thermodynamic property calculations by different authors [55–58] and according to Müller and Gubbins [59] more than 200 published articles have used SAFT-type equations. Compared to the SAFT model, the PC-SAFT model has improved the dispersion term by applying a perturbation theory for chain molecules and consequently the model representation of phase equilibria data [43]. This has been one of the SAFT model modifications with numerous use observed in literature and in chemical industries.

Detailed analysis of SAFT equations for different kinds of compounds can be found in the literature [60–64]. On the other hand, PC-SAFT equation gives better results than cubic EoS (SRK and PR with Peneloux volume corrector [65]) for prediction of gas phase compressibility factors and oil phase compressibility [60]. Also, it is known that SAFT EoS has difficulties in representing the critical properties (pure and mixture) properly [61]. A renormalization group theory was proposed by White [66,67] and has been applied to SAFT-types equation, for example those by Mi et al. [68] and Llovel et al. [69] aiming to correct properties values in the area of the critical properties. PC-SAFT equations were also analyzed by Privat et al. [61,62]. The authors [61] proposed an algorithm capable to detecting more than three molar volume roots once it was found that PC-SAFT equation can exhibit up to five different volume roots while cubic equations give at the most three volume roots. It is know that only one or two volume roots have real significance. Deficiencies found for SRK (second critical point) and SAFT equations (five different volume roots, second critical point) were pointed by different authors [33,70–76] and are also described in Privat et al. [61]. The problem found for the unrealistic volume roots were also observed for SLE systems at low temperature, which can present unrealistic SLE predictions, multiple eutectic points and liquid-liquid azeotropy [62]. The authors [62] also confirmed the importance of the binary interaction parameters (k_{ij}) for the correct representation of the phase equilibria

data, especially in order to avoid the problem of unrealistic volume roots. Nevertheless, PC-SAFT should be used with caution in systems at high-pressure with polar compounds [77]. It was identified that SAFT and its derivatives such as PC-SAFT have two problems in predictions of the experimentally available data: i) the temperature dependencies of a segment packing fraction, which are responsible for predicting the intersection of isotherms at high densities; ii) the very high-polynomial order by volume, which results in negative values of the heat capacities at extremely high pressure [78].

PC-SAFT equation of state combined with Group-Contribution (GC) methods

Prediction of the pure component parameters utilizing PC-SAFT equation of state combined with Group-Contribution (GC) was proposed by Privat et al. [61]. The proposed parameters were utilized to generate pseudo-experimental data for the temperature dependent properties for regression of the GC-based model parameters for edible oil and biodiesel compounds [79]. For mixtures, Group-Contribution (GC) methods combined with equations of state for the binary interaction parameter calculation and can be found in literature for SRK and PR for example in the works of Holderbaum and Gmehling [80], Ahlers and Gmehling [81], Jaubert and Mutelet [82], Vitu et al. [83] and Privat et al.[84]. SAFT equation was combined with GC for hydrocarbon compounds by Tamouza et al. [85]. The authors [86] also extended the work after for binary mixtures of alkanes and alcohols, and polar compounds [87]. GC-PPC-SAFT for ammonia and its mixtures is proposed by Grandjean et al. [88], for hydrocarbons at pressures to 276MPa and temperatures to 533k by Burgess et al. [89] and for light and heavy esters by Thi et al. [90]. Molecular parameter estimation utilizing group-contribution for pure component and mixtures was also proposed by Vijange et al. [91,92], Emami et al. [93] for PC-SAFT and Tihic et al. [94] for simplified PC-SAFT.

Modelling of associative compounds and their mixtures

For associating systems, such the ones containing alcohols, amines and acids, different EOS were analyzed by Gross and Sadowski [95], Muller and Gubbins [59], Tumakaka and Sadowski [96], Veytsman [97] and Wei and Sadus [98]. Also considered for associating mixtures is the Cubic Plus Association (CPA) [99], based on the

combination of SRK equation with the Wertheim theory for the polar/association terms. The CPA-EOS has been used by various authors with similar results found for PC-SAFT.

Michelsen [100] proposed a robust solution for the use of association models, solving the problem of the complexity observed while considering the association term. Michelsen work [100] brings detailed equations for association scheme 1A (one associate side – generally indicated for acids), association scheme 2B (two association side with opposite polarity – generally indicated for alcohols), and association scheme 3B (two identical sides shows one polarity and the third side shows the opposite polarity – generally indicate for alcohols). Michelsen [100] also commented that the association scheme 4C (two association sides of each polarity – generally indicated for water and glycols) behaves similar to the 2B scheme. For systems containing water, Huang and Radosz [41] considered three associating sides for the molecule and Gubins et al. [101,102] have considered four associating sides and Gross and Sadowski [44] have considered two associating sides for all associate substances with good results.

In PC-SAFT equation, two more pure component parameters are considered for associating systems, the association energy $\varepsilon^{A_iB_i} / k$ and the effective association volume $\mathrm{K}^{A_iB_i}$. For heavier alcohols than methanol, Von Solms et al. [103] showed using spectroscopy that 2B can be generally used. The same (2B for heavier alcohols than methanol) was also considered by Wolbach and Sandler [104]. Huang and Radosz [41] considered two associating sides (2B) for any kind of alcohol. Laffite et al. [105] have compared 2B and 3B for different kinds of alcohol. For carboxylic acids, the association scheme 1A was considered by Huang and Radosz [41] and by Fu and Sandler [106]. Yushu et al. [107] and [108] considered two associating sides for carboxylic acids. Finally, for esters Soo [109] used non-polar PC-SAFT to calculate density and the non-polar GC-SAFT was also utilized for ester by Thi et al. [90]. Von Solms el al. [110] considered esters as self-associating to improve model representation of simplified-PC-SAFT.

SAFT model and its modifications analysis in describing lipids systems

SAFT and PC-SAFT EOS were parameterized for a wide range of compounds including organic, polymers, and water to low and high pressure [41–44,95]. However, for lipids systems, many of the needed parameter values are missing. For biofuel systems,

modelling of thermodynamic properties using PC-SAFT and the analyze of different molecular structures and interactions has been reported by Soo [109]. Tihic [111] has used GC simplified PC-SAFT for the calculation of vapour pressure and phase equilibria of fatty acid esters. Oliveira et al. [112] have used soft-SAFT model to predict different properties, such as density, viscosity and surface tension. The same model (soft-SAFT) was used to describe systems containing biodiesel with water and alcohols by the group [113]. Dong et al. [114] used PC-SAFT model combined with group-contribution method to predict density of biodiesel. Higher fatty acids form cyclic dimmers due the presence of the negatively polarized oxygen atom from the carbonyl group and the positively polarized hydrogen atom from the carboxyl group [115]. Perdomo et al. [116] have used SAFT-VR to predict vapour pressure and liquid density of biodiesel compounds. SAFT combined with a group contribution method (SAFT-γ) was used to predict biodiesel properties as vapour pressure, liquid and vapour density and boiling point by Perdomot et al. [117].

Problems in the PC-SAFT calculation of density was observed for water in the work of Song et al. [118]. It was also observed the tendency of PC-SAFT model in over predict the density of hydrocarbons [119,120]. For heat capacity calculation, Villiers et al. [121] have showed that PC-SAFT gives accurate prediction for alkanes in comparison with SAFT and CPA at the temperature and pressure range studied.

2.2.4 Thermodynamic consistency tests

An important issue related to the modelling of phase equilibria is the evaluation of measured data-sets used in the parameter regression step. The evaluation approach used by Gmehling et al. [122] involves the application of various thermodynamic consistency tests and then screening of experimental VLE data-sets based on strict pass/fail criteria. However, such an approach requires personal judgment of an expert and may result in rejection of large portions of experimental data-sets [123]. A more general and robust approach is developed by the Thermodynamics Research Center (TRC) of the National Institute of Standards and Technology (NIST) in which a single numerical quality factor Q_{VLE} is evaluated and assigned for each VLE data-set based on various thermodynamic consistency tests. These Q_{VLE} values are then used as weighting factors (better quality means higher weight and more reliability) in the regression of UNIFAC binary

interaction parameters [123]. Using this approach it is possible to use all of the available VLE data-sets in the parameter regression.

For assessing the quality of the VLE data, many consistency tests, mostly derived from the Gibbs-Duhem equation, have been proposed (Van Ness [124], Herington [125], Mc Dermott and Ellis [126], Christiansen and Fredenslund [127], Kojima et al. [128], Wisniak [129], Wisniak and Tamir [130], to name a few). In this work, the consistency tests developed by NIST were considered since these are the most commonly employed. A detailed description and application of these tests is given by Kang et al. [131].

The program ThermoData Engine (TDE) developed at NIST by Frenkel et al. [132–138] does not reject any VLE data-set found to be inconsistent [131]. Rather, it assigns a lower weight (quality factor) to that data-set. If a test fails, the corresponding qualitative test assigns a value for its quality factor $Q_{test,i}$ (for i=1, 6) ranging from 0.1 to 1, where,

$$Q_{test1} + Q_{test2} + Q_{test3} + Q_{test4} + Q_{test5} + Q_{test6} = 1 \tag{10}$$

For VLE data-sets, the description of thermodynamic consistency tests that provide quality factors, $Q_{test,i}$, is given in Table 1.

The Van Ness test (Q_{test1}) checks how the measured data (TPxy) represent the thermodynamic models. The pressure and the vapour phase composition are calculated using a thermodynamic model (for example, NRTL, UNIQUAC, UNIFAC etc.) within a bubble-point calculation. In the area or Herington test (Q_{test2}) the integration of the Gibbs-Duhem equation is considered for TPxy data. The activity coefficients are calculated by an appropriate property model, for example, any GE-based model. In Point or Differential Test (Q_{test3}), the differential properties of excess Gibbs free energy are considered for TPxy data. Typically the integration term ε is less than 3.10-5 [124]. But for isobaric systems it is significant and should be considered. The equation for the term ε is given in Table 1. More details about the empirical estimate of the excess enthalpy (H^E) using the total boiling range of the mixture are given by Herington [125]. Infinite Dilution test (Q_{test4}) consider the limiting behaviour of $\frac{G^E}{x_1 x_2 RT}$ and the activity coefficients γ_1 and γ_2. In pure component consistency test (Q_{test5}), the consistencies of the end-points (x=0 and 1) of the VLE data are considered by comparing these values with their pure component vapour pressures. The advantage of this test is that it is also applicable for TPx or TPy data. Finally, for equations of state

(EoS) based models (for example, Peng-Robinson EoS), test-6 (Q_{test6}) is applied, for data at high-pressure (>1MPa) and not too close to the critical point. Note that if a test is not performed, its corresponding quality factor in Eq. 10 is set to zero. The scheenshot of the ThermoData Engine (TDE) program can be seen in Figure 6.

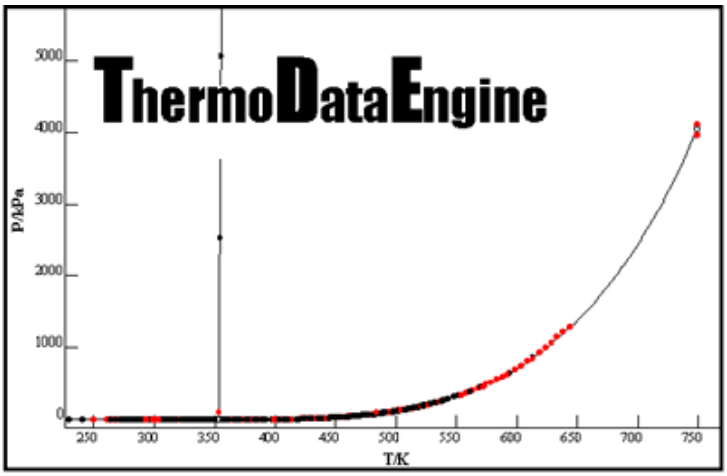

Figure 6: Scheenshot of the ThermoData Engine (TDE) program.

Marcilla et al. [139] have reported pitfalls in the evaluation of the thermodynamic consistency tests proposed for VLE data. The authors [139] demonstrated that Herington approximation for the area test (Q_{test2} in TDE program [132–138]) can erroneously classify a data set as inconsistent, or validate erroneous data - as also pointed by Wisniak [140]. Important discussion regarding the model representation (considering NRTL model) of the experimental data using Van Ness test (Qtest,1 in TDE program [132–138]) were added by the Marcilla et al. [139]. Before apply Q_{test1}, it is important to guarantee that the thermodynamic model (such NRTL, UNIQUAC, etc) can represent the class of experimental data before the test be applied, as also reported by Jackson and Wilsak [141].

Table 1: Quality factor present in the VLE thermodynamic tests.

VLE thermodynamic consistency tests	Quality factor
Van Ness Test	$Q_{test1} = \frac{2}{\Delta P + \Delta y}$ for ΔP and Δy between 1 and 10
Area Test (Herington Test)	$Q_{test2} = \frac{5}{D}$, for isothermal systems and D between 5 and 50
	$Q_{test2} = \frac{10}{\lvert D - J \rvert}$, for isobaric systems and $\lvert D - J \rvert$ between 10 and 100
Point or Differential Test	$Q_{test3} = \frac{5}{\delta}$, for δ between 5 and 50
	Where: $\delta = \frac{100 \sum_{k=1}^{N} \delta_k^*}{N}$
	And $\delta_k^* = \left[\frac{d\left(\frac{G^E}{RT}\right)}{dx_1} - \ln\left(\frac{\gamma_1}{\gamma_2}\right) - \varepsilon \right]_k$
	$\varepsilon = \left(\frac{V^E}{RT}\right)\left(\frac{\partial P}{\partial x_1}\right)_T$ for T constant $\varepsilon = \left(\frac{H^E}{RT^2}\right)\left(\frac{\partial T}{\partial x_1}\right)_P$ for P constant
Infinite Dilution Test:	$Q_{test4} = \frac{60}{I_1 + I_2}$, for I_1 and I_2 between 30 and 300
	$I_1 = 100 \left\lvert \frac{\left(\frac{G^E}{x_1 x_2 RT}\right) - \ln\left(\frac{\gamma_1}{\gamma_2}\right)}{\ln\left(\frac{\gamma_1}{\gamma_2}\right)} \right\rvert_{x_1=0}$ $I_2 = 100 \left\lvert \frac{\left(\frac{G^E}{x_1 x_2 RT}\right) - \ln\left(\frac{\gamma_1}{\gamma_2}\right)}{\ln\left(\frac{\gamma_1}{\gamma_2}\right)} \right\rvert_{x_2=0}$
Pure component Test	$Q_{test5} = \frac{2}{100\left(\Delta p_1^0 + \Delta p_2^0\right)}$, for Δp_1^0 and $\Delta p_2^0 \geq 1$
Equation of state (EOS) Test	$Q_{test6} = \frac{3}{\Delta P + 100\ \Delta y}$

It is important to note that, thermodynamic consistency tests reported in the literature for evaluation of the quality of measured LLE and SLE data-sets for lipids systems were not found. Null [142] proposed a thermodynamic consistency test for SLE systems using a relation between the solid and liquid activity coefficients for systems containing metals, where the data from the two phases are given, that is not the case for the data sets found for lipids.

2.2.5 Iodine value and cloud point estimation for lipids

The iodine value, between other physical-chemical properties of vegetable oils, can differ according to the weather conditions during the growth of the plant, hybridization species, time of the crop examination, or storage period [143]. Iodine value considers the quantity of unsaturated compounds present in the vegetable oil and fats in the form of double bonds and can be quantified by the mass of iodine in grams consumed by 100 grams of the substance. Some authors [144–148] have reported iodine value correlation with fatty acids composition, and observed that the iodine value increases when linoleic acid increases and oleic and saturated acids decreases. Palm oil is one of the vegetable oils with high production and consumption [149] and differs from other vegetable oils in composition of fatty acids. Palm oil consists of two phases in normal conditions of temperature (25°C) that can be cooled and separated into olein and stearin, what makes iodine value and melting point important properties for this oil. For biodiesel production, the iodine value is limited to 115g in the European standard UNE-EN 14214 [150]. This limitation is necessary once heating higher unsaturated fatty acids results in polymerization of glycerol that form deposits or deterioration of the lubricating [151]. Therefore, a model calculation for iodine value that considers the composition of the compounds could be profitable for vegetable oils and biodiesel. Knothe [152] proposed a model for iodine value that considers the double bonds quantity and the molecular weight values. For fatty acid methyl esters, Kyriakidis and Katsiloulis [153] proposed a method to calculated iodine value from the composition of mono-, di-, and tri-unsaturated fatty acid methyl esters. Ham et al. [154] have showed good correlation of experimental iodine value for marine oil and the calculated values using the composition of the fatty acids and their iodine values (pure property).

Cloud point values indicate when the mixture begins to crystallize under controlled cooling and it is also related with the unsaturation of the mixture. For biodiesel, high

values of cloud point make the use of pure biodiesel challenging in colder climates. In vegetable oils and biodiesel, when the concentration of unsaturated compounds increases, the cloud point decreases. A correlation between the predicted cloud point of the palm oil (both olein and stearin fractions) and iodine values was showed by Zaliha et al. [155]. For binary mixtures, the cloud point was calculated considering the SLE by Imahara et al.[156], Iyer [157] and Lopes et al. [158]. A prediction that do not consider a thermodynamic correlation for cloud point calculation was made considering the molecular weight, the melting point for the pure component and adjusted parameters given by Sadeghazad and Sobhi [159] for binary mixtures including paraffin. The cold filter pluggling point (CFPP), another property for biofuels, can be calculated using a linear relationship with cloud point by Iyer [157] and Dunn and Bagby [160]. The same property (CFPP) was correlated with iodine value by Moser [161]. Saiban and Brown [162] have showed the cloud point calculation for blends of diesel fuel. Sarin et al. [163] proposed a method to calculated cloud point for blends of palm, jatropha and pongamia biodiesels from the total unsaturated fatty acids methyl esters composition. Su et al. [164] showed good results in the representation of cloud point for biodiesel compounds considering the weighted-average number of carbon atoms, weighted-average number of double bonds, and composition of unsaturated fatty acid methyl esters in the biodiesel, plus two regressed coefficients. Iodine value and the cloud point were correlated for blends of palm olein and olive oil by Naghshineh et al. [165]. Any method that correlate iodine value and cloud point applied for different vegetables oils and biodiesel could be found in literature.

2.2.6 Experimental work procedure

In edible oil/fat and biodiesel production, modelling, simulation and design of unit operations require knowledge of phase equilibria in VLE, LLE as well as SLE circumstances. Refining of oils/fats involves a crucial stripping step named steam deacidification/deodorization in which undesirable compounds, such as free fatty acids and odors (aldehydes, hydrocarbons and ketones) are removed based on differences in their volatility in relation to triacylglycerols. In conjunction with this desirable removal, there is also an undesirable loss of neutral oil (mono-, di-, and triacylglycerols) due to volatilization [166,167]. In the purification steps of biodiesel and bioglycerin, partial acylglycerols (mono- and diacylglycerols) formed in the transesterification reaction are

removed from a mixture of fatty esters or glycerol. Knowledge of the VLE involved in these steps is fundamental for understanding the behaviour of these chemicals under the processing conditions [168]. Ceriani et al. [169] indicated a lack of experimental data of thermophysical properties of pure fatty compounds and their mixtures. Recently, Matricarde Falleiro et al.[170,171], Akisawa Silva et al. [172,173], and Damaceno et al. [168] measured vapour pressures/boiling temperatures of pure fatty compounds and binary fatty systems using DSC (differential scanning calorimetry) technique. Figure 7 brings an example of endoterms from Matricarde Falleiro et al. [170] and Figure 8 shows the Differential Scanning calorimetry (DSC) utilized during the experimental work.

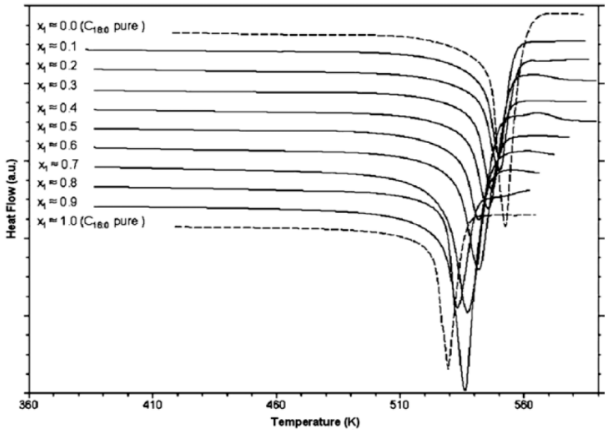

Figure 7: Boiling endoterm given by DSC technique to determine the boiling point or onset temperature.

Figure 8: Differential Scanning Calorimetry (DSC) utilized during the experimental work.

The use of DSC technique for measuring thermophysical properties of fatty systems is increasing due to its clear advantages i.e., it uses very small samples, 3-5 mg in comparison to ebulliometry (cost-effective) and it provides the results in a shorter operation time, avoiding thermal degradation of compounds prior to Vapourization. For each mole fraction of the liquid phase, DSC technique shows a boiling endoterm, aiming determines the boiling point or onset temperature.

Other equipment used in VLE measurements is Ebulliometer Fisher. Its operation is based in the circulation method that allows the contact between the liquid and vapor until the equilibrium condition has been achieved. Part of the liquid of the mixture is evaporated by an electrical immersion heater installed in the glass apparatus. The mixture is separated in liquid and vapor in a separation chamber and constant recycling of liquid phase and condenser phase at simultaneous mixing of the recirculated flows in the mixing chamber active the equilibrium that are measured in the stationary conditions. The composition of the samples can be determinate using chromatography techniques.

Chapter 3. Database

Lipids are often not tabulated in common property databases and their polyfunctional structure requires careful model analysis. The compounds, processes and types of phase equilibrium of interest in this project were defined prior to data collection, as shown in Figure 9. Also, it was defined that first binary data would be considered in the model analysis, followed by ternary and multicomponent data.

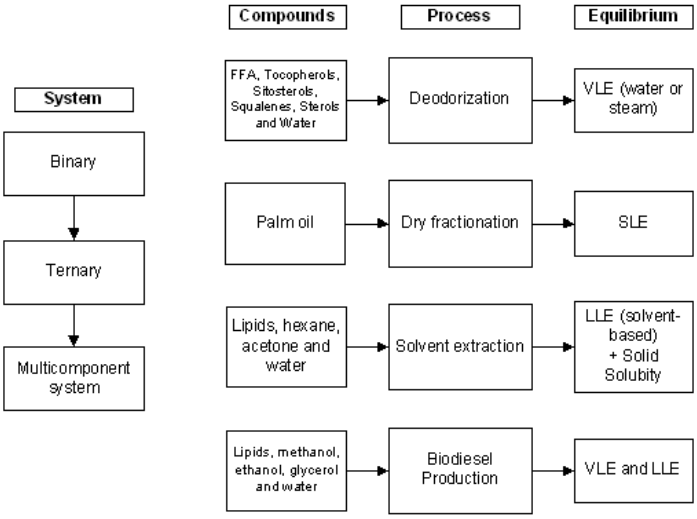

Figure 9: Compounds, processes and types of phase equilibrium of interest in this project.

Property model development requires reliable data and their evaluation. For the purposes of this work, a search of the literature was made to collect, within a limited time, as many data as possible. The criteria for data selection were details of measurement technique, measurement accuracy, different ranges of temperature, pressure, and molar fractions considered by the authors reporting these experimental data. The collected data are unlikely to be all those in the literature. However, the database is fully adequate to develop and test physical property models for the classes of lipids treated in this work.

One of the first tasks of this project was the development of a database (CAPEC_Lipids_Mixture_Database) containing measured data of mixture properties. Currently, there are 333 different phase equilibrium systems (which include 92 VLE, 91 LLE, and 70 SLE systems), and 80 solid solubility systems. The total number of data-points of properties related to phase equilibria is 4500. Table 2 brings details of the phase equilibrium systems present in the mixture database for lipids. The collected SLE data of lipids (CAPEC_Lipids_Mixtures_Database) provides saturation compositions of solid compounds in solution at specific temperatures. Finding the solid structure and/or considering its effect on the saturation composition of the liquid, is not an objective of this particular work. Rather, because of measurement uncertainties or quality estimates are unavailable for many literature experimental data, the focus is on the analysis of data quality for systems where the solid is probably well characterized. The data for some acylglycerols are not available in the database, due to the difficulties in measuring their properties. The activity coefficient values predicted using different well-known G^E models (NRTL, UNIQUAC, and original UNIFAC) for different lipid systems are also stored in the database for their use in phase equilibria calculations. In Appendix 1, the available information in the database, including the phase equilibria properties for binary and multicomponent systems are given.

Table 2: Phase equilibrium systems present in the mixture database for lipids (CAPEC_Lipids_Mixture_Database).

Compound	Carbon length	Phase equilibrium																Thermodynamic consistency test (Q factor)	
		VLE						LLE						SLE		Solubility		VLE	SLE
Fatty		Binary	Mult.	Isobaric	Isothermal	PTX	PTXY	Binary	Mult.	Isobaric	Isothermal	PTX	PTX[1]X[2]	Binary	Mult.	Binary	Mult.		
Fatty Acids	C5 – C20	19	2	20	1	2	19	3	4	7	-	6	1	20	10	48	5	0.0034 - 0.680	0.005 - 0.995
Methyl Esters	C6 – C18	20	1(+3VLLE)	19	2(+2VLLE)	14	9(+1VLLE)	1	15	15	1	3	13	7	-	19	-	0.027 - 0.500	0.019 - 0.194
Ethyl Esters	C10 - C18	7	-	2	2	2	5	-	3	3	-	-	3	9	-	1	-	0.024 - 0.500	0.017 – 0.051
Acylglycerols																			
Monoacylglycerol	C10-C12	-	-	-	-	-	-	-	-	-	-	-	-	2	-	-	-	-	-
Diacylglycerol	C20-C32	-	-	-	-	-	-	-	-	-	-	-	-	4	-	-	-	-	-
Triacylglycerol	C27-C57	2	-	1	1	-	2	-	7	7	-	-	7	18	-	6	-	-	-
Pseudo-compounds																			
Vegetable oil	C48-C58	2	-	-	2	2	-	2	43	45	-	7	38	-	-	1	-	-	-
Biodiesel	C14-C24	1	-	-	-	1	-	1	10	10	1	4	7	-	-	-	-	-	-
Minor compounds	C28-C53	2	2	2	2	2	2	-	-	-	-	-	-	-	-	-	-	-	-
Other compound (glycerol)[1]	C3	30	1	24	4	25	6	2	-	2	-	2	-	-	-	-	-	0.0045 - 0.500	-
Sub Total		83	9	68	16	48	44	9	82	89	2	22	69	60	10	75	5	-	-
Total		92						91						70		80		-	-

[1]Since it is present in biodiesel production, it is included in this work.

Chapter 4. Property model analysis

The model analysis for lipid systems, includes the models - NRTL, UNIQUAC and UNIFAC model, which have been described in section 2.2.1 of Chapter 2. With respect to improvement of the model performance, original UNIFAC and PC-SAFT models were considered. For the model parameter estimation step, various options of objective functions were considered, accounting for uncertainties present in the experimental data. The selection of appropriate thermodynamic models is extremely important for an accurate description of the phase equilibria. In addition, with the selection of appropriate thermodynamic models, the consistency of the experimental data should also be considered to obtain accurate physical and thermodynamic properties. The existing pure component database for lipids (CAPEC_Lipids_Database) and the mixture database for lipids (CAPEC_Lipids_Mixture_Database) have been combined together with the quality factors obtained from the thermodynamic consistency tests from TDE program [132–138] for VLE data and considering the new thermodynamic consistency tests for SLE data. Also, the regressed parameters for NRTL, UNIQUAC and original UNIFAC have been added, extending the lipids database. The information of the quality factors and parameters for each data set considered for VLE and SLE of systems involving lipids is provided as a supplementary material (Appendix 4).

4.1 Evaluation of GE model performance

The measured phase equilibrium data is analyzed using thermodynamic consistency tests and performances of well-known thermodynamic models (NRTL, UNIQUAC, and original UNIFAC) are evaluated for different lipid mixture systems. In Table 3, the performances of the NRTL, the UNIQUAC and the original UNIFAC models in predicting VLE data are compared for selected lipids system. For NRTL and UNIQUAC, parameter regression is performed to fine-tune the existing model parameters to improve the VLE prediction as well as to estimate the model parameter values that are not available in the literature. Also in Table 3, the performance of the original UNIFAC model is given based on the published parameter values [17]. The values of estimated temperature dependent parameters for the NRTL and the UNIQUAC model for the listed lipid systems are also given in Table 3. In Table 4, the

performances of the models for prediction of SLE data are compared. Larger deviations in the predicted mixture temperatures are observed for the original UNIFAC model in comparison with NRTL and UNIQUAC models. Similar observations have been reported by Coelho et al. [9].

Table 3: VLE model performance statistics for lipid systems.

	Temperature ARD (%)	Vapour molar fraction ARD .10^2	Parameters A_{12}/K[1]	A_{21}/K[1]	α_{12}[1]	Reference
Hexanoic acid (1) + octanoic acid (2) (388.95 to 405.15 K and 2700 Pa)						
NRTL	0.077	0.966	565.96	-569.50	0.2	[174]
UNIQUAC	0.094	0.861	-558.49	530.99	-	
Orig. UNIFAC	0.079	0.980	-	-		
Lauric acid (1) + myristic acid (2) (427.15 to 447.15 K and 500 Pa)						
NRTL	0.159	2.370	5572.64	-1992.14	0.55	[174]
UNIQUAC	0.154	2.310	5940.85	-2734.18	-	
Orig. UNIFAC	0.336	0.901	-	-	-	
Palmitic acid (1) + stearic acid(2) (523.71 to 545.63 K and 6666.12 Pa)						
NRTL	0.247	2.360	9916.65	470.78	1.37	[170]
UNIQUAC	0.258	2.550	10075.92	-3845.46	-	
Orig. UNIFAC	0.508	1.582	-	-	-	
Methyl myristate(1) +methyl palmitate(2) (523.71 to 545.63 K and 6666.12 Pa)						
NRTL	0.107	3.28	537.01	5731.60	2	[175]
UNIQUAC	0.130	4.015	-2640.48	5552.49	-	
Orig. UNIFAC	0.534	2.838	-	-	-	
Methyl palmitate(1) +methyl stearate(2) (469.15 to 491,15 K and 5300 Pa)						
NRTL	0.410	3.56	-173.65	-1799.80	2	[176]
UNIQUAC	0.412	3.74	3648.76	-3545.23	-	
Orig. UNIFAC	0.942	1.40	-	-	-	
Ethyl palmitate(1) + ethyl stearate(2) (502.27 to 520.56 K and 5332.9 Pa)						
NRTL	0.292	5.081	8298.72	6557.63	1.29	[172]
UNIQUAC	0.379	4.892	1333.45	441.70	-	
Orig. UNIFAC	2.030	1.801	-	-	-	

[1] Aij/K and α_{12} are the binary molecular parameter for the compounds i and j.

Table 4: SLE model performance statistics for lipid systems.

	Temperature	Parameters						
	ARD (%)	A_{12}/K[1]	A_{12}/K[2]	A_{21}/K[1]	A_{21}/K[2]	α_{12} [1]	α_{12} [2]	Reference
Lauric acid (1) + myristic acid (2) (316.94 to 327.48 K and 101300 Pa)								
NRTL	0.102	-6719.60	-7476.75	35.98	448.67	0.97	0.31	[177]
Orig. UNIFAC	0.289	-		-		-		
Myristic acid (1) + palmitic acid (2) (327.07 to 335.02 K and 101300 Pa)								
NRTL	0.062	574.25	755.89	-4570.86	4618.88	-0.49	-0.33	[178]
Orig. UNIFAC	0.098	-		-		-		
Methyl Palmitate (1) + methyl Stearate (2) (303.93 to 314.07 K and 101300 Pa)								
NRTL	0.329	243.23	1096.17	-275.42	-1319.24	2.00	2.00	[179]
Orig. UNIFAC	0.337	-		-		-		

[1] Aij/K and α_{12} are the binary molecular parameter for the compounds i and j before the eutectic point. [2] Aij/K and α_{12} are the binary molecular parameter for the compounds i and j after the eutectic point.

It is important to note that, for SLE systems containing eutectic and peritectic point, two regions are defined and the parameter regression for the NRTL and UNIQUAC models are then performed for each region.

Figures 10-11 show the performance of the selected models for VLE predictions while Figures 12-13 show the performance of the same models for SLE predictions. Figures 10-13 show that the original UNIFAC model did not perform as well as the NRTL and the UNIQUAC models for the prediction of VLE and SLE data. The main reason is due to the fact that the original UNIFAC-VLE model parameters were not regressed with only data from lipid systems. One way to improve the performance of the original UNIFAC model for lipid systems is to fine-tune the model parameters with the VLE data-sets of lipids systems together with quality factor from consistency tests

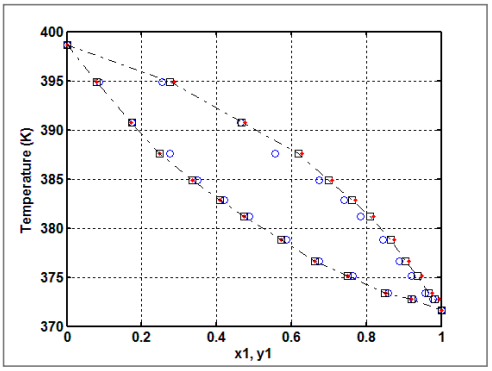

Figure 10: VLE of hexanoic acid(1) + octanoic acid(2) for 1.3KPa. Experimental work [174] (○); NRTL model (□); UNIQUAC model (*); original UNIFAC model(-.-).

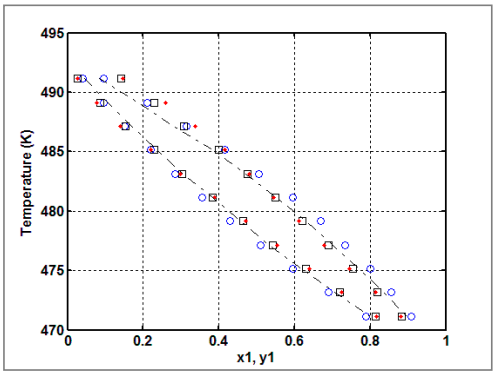

Figure 11: VLE of methyl myristate (1) + methyl palmitate(2) for 1.3KPa. Experimental [176] (○); NRTL model (□); UNIQUAC model (*); original UNIFAC model(-.-).

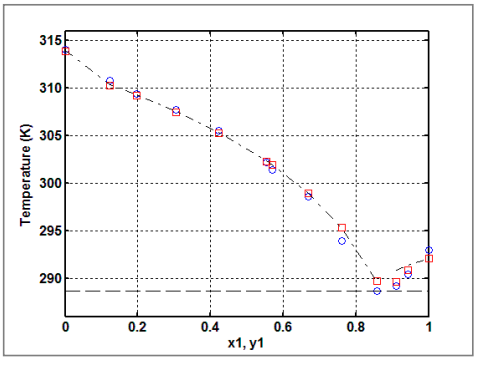

Figure 12: SLE of methyl myristate(1) + methyl stearate(2) for 1.3KPa. Experimental work [179] (○); NRTL model (□); orig. original UNIFAC model(-.-).

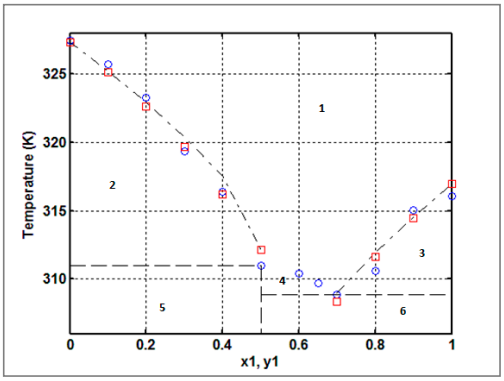

Figure 13: SLE of lauric acid(1) + myristic acid(2) for 1.3KPa. Experimental work [177] (○); NRTL model (□); original UNIFAC model(-.-).

Note: Region 1 represents the liquid phase, region 2 the solid myristic acid coexisting with the liquid phase, region 3 the solid lauric acid coexisting with the liquid phase, region 4 a solid mixture phase coexisting with the liquid mixture phase, region 5 the solid mixture phase coexisting with the pure solid lauric acid and finally, region 6 a solid mixture phase coexisting with the pure solid myristic acid.

Table 5 gives the results of the regression for selected lipid systems. For isobaric systems, it is important to note that the pure component vapour pressure model may also affect the VLE calculations and consequently the parameter regression of the GE model. This is illustrated for the selected system for which VLE data was found in the literature [174]. In Table 5, the regression statistics are given for these data-sets at three different pressures. Note that only data-set 3 passed the Van Ness test (Q_{test1}). Figure 14 shows the temperature deviations for the selected data-set of the lipid system-(decanoic acid + lauric acid).

Table 5: Average relative deviation (ARD%) for the original UNIFAC parameter regression calculations for VLE lipid systems [174].

Data-sets	Pressure (Pa)	Temperature	Vapour molar fraction	Parameters	
		ARD (%)	ARD .10^2	A_{12}/K[1]	A_{21}/K[1]
Hexanoic acid (1) + octanoic acid (2) (372.56 to 444.63 K)					
1	400	0.08	1.60	-7241.89	-594.34
2	1330	0.09	2.02		
3	6700	0.10	0.89		
4	13300	0.07	1.28		
Improvement in the minimum value of objective function: 4.92 E-05					
Decanoic acid (1) + lauric acid (2) (405.82 to 497.37 K)					
1	500	0.37	3.04	9985.20	4331.01
2	2500	0.12	0.82		
3	13300	0.14	0.482		
Improvement in the minimum value of objective function: 3.83 E-02					
Lauric acid (1) + myristic acid (2) (423.29 to 501.56 K)					
1	400	0.42	1.77	-6288.99	-5506.40
2	530	0.36	4.76		
3	6700	0.10	0.89		
4	13000	0.18	1.74		
Improvement in the minimum value of objective function: 1.08 E-02					

[1] Aij/K and α_{12} are the binary molecular parameter for the compounds i and j.

For modelling of SLE of lipid systems, it is found that the performance of the original UNIFAC model is not as good as that of the NRTL model. Hence, fine-tuning of the original UNIFAC model parameters is done using the SLE data-sets of lipids systems and using the quality factors obtained from the consistency tests developed in this work for SLE systems. Table 6 gives the performance statistics for three different lipid systems analyzed. It can be observed from Table 6 that, inclusion of lipids systems in the regression has improved the minimum value of objective function.

Table 6: Average relative deviation (ARD%) for the original UNIFAC parameter regression calculations for SLE lipid systems.

Data-sets	Temperature ARD (%)	Parameters A_{12}/K[1]	A_{21}/K[1]	A_{12}/K[2]	A_{21}/K[2]
Lauric acid (1) + myristic acid (2) (278.36 to 328.88 K and 101300 Pa)					
1 Costa et al. [177]	0.22				
2 Boros [180]	9.45	-9572.48	-6717.89	-4621.70	-38837.98
3 Costa [181]	0.21				
Improvement in the minimum value of objective function		1.04 E-03		4.42 E-03	
Myristic acid (1) + stearic acid (2) (320.68 to 343.98 K and 101300 Pa)					
1 Boros [180]	0.26	-9526.58	-7225.01	-8754.77	-4770.20
2 Costa [181]	0.38				
Improvement in the minimum value of objective function		3.21 E-06		1.76 E-04	
Methyl palmitate (1) + methyl stearate (2) (294.97 to 314.07 K and 101300 Pa)					
1 Boros [180]	1.57	-8395.93	2375.11	-9987.93	-5676.50
2 Costa et al. [179]	0.48				
Improvement in the minimum value of objective function		1.71 E-04		3.12 E-06	

[1] Aij /K are the binary molecular parameter for the compounds i and j before the eutectic point. [2] Aij /K are the binary molecular parameter for the compounds i and j after the eutectic point.

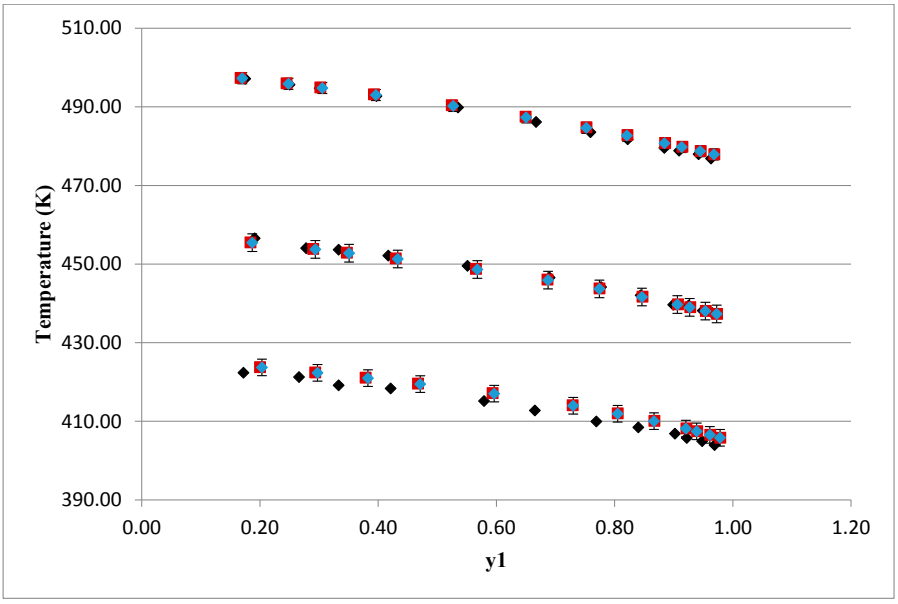

Figure 14: VLE of decanoic acid + lauric acid. ◆Experimental work [41], ■Original UNIFAC model and ◆Parameter regression.

The parameters obtained in the regression considering NRTL, UNIQUAC and original UNIFAC model for lipids systems are given in Appendix 2. In this work, the external tool MoT (Modelling Testbed) available in the software ICAS® (Integrated Computer Aided System) developed in CAPEC center was used in this regression. The equations for the cited thermodynamic models (NRTL, UNIQUAC, and original UNIFAC) were now extended to include parameter regression and attend VLE, SLE and LLE systems. The code for MoT is given in Appendix 3.

4.1.1 Analysis of combinatorial and residual terms

Aiming analyze the reason of the higher deviations observed for original UNIFAC in comparison with NRTL and UNIQUAC model, the combinatorial and residual terms of original UNIFAC and UNIQUAC models were analyzed separated. Two different examples for lipids were selected to illustrate this comparison and are given in Table 7 and 8.

Table 7: Comparison between combinatorial and residual terms for UNIQUAC and original UNIFAC models. Experimental data: lauric acid and myristic acid at 0.53KPa [176].

UNIQUAC model				Original UNIFAC model			
Residual γ	Comb. γ	γ 1	$\lvert\gamma$ exp- γ calc$\rvert$	Residual γ	Comb. γ	γ 1	$\lvert\gamma$ exp- γ calc$\rvert$
0.737	0.994	0.733	0.070	0.948	0.994	0.947	0.279
0.745	0.994	0.741	0.142	0.949	0.995	0.944	0.346
0.854	0.997	0.851	0.064	0.971	0.997	0.968	0.181
0.891	0.998	0.889	0.029	0.979	0.998	0.976	0.117
0.950	0.999	0.949	0.057	0.990	0.999	0.989	0.097
0.988	0.999	0.988	0.027	0.998	0.999	0.997	0.037

Table 8: Comparison between combinatorial and residual terms for UNIQUAC and original UNIFAC models. Experimental data: ethyl palmitate and ethyl oleate at 9.33 KPa [172].

UNIQUAC model				Original UNIFAC model			
Residual γ	Comb. γ	γ 1	$\lvert\gamma$ exp- γ calc$\rvert$	Residual γ	Comb. γ	γ 1	$\lvert\gamma$ exp- γ calc$\rvert$
1.910	0.998	1.907	0.761	1.332	0.998	1.329	0.184
1.338	0.998	1.336	0.488	1.271	0.998	1.269	0.421
1.101	0.999	1.099	0.181	1.213	0.999	1.211	0.293
1.002	0.999	1.001	0.031	1.166	0.999	1.160	0.128
0.968	0.999	0.967	0.095	1.115	0.999	1.114	0.051
0.963	0.999	0.963	0.067	1.080	0.999	1.079	0.049
0.973	1.000	0.972	0.006	1.046	1.000	1.046	0.067
0.985	1.000	0.985	0.023	1.022	1.000	1.022	0.061
0.996	1.0000	0.996	0.016	1.006	1.0000	1.006	0.025

It is possible to observe that original UNIFAC model have the tendency to underestimate the values of activity coefficient (γ) for lipids systems. As expected, the residual part of the activity coefficient has determined the variation observed between UNIQUAC and original UNIFAC models. Also, for the data set containing the mixture

of two fatty acids (Table 7), original UNIFAC shows values of activity coefficients close to the ideality and do not consider the interaction between the two compounds.

4.1.2 Objective functions for parameter regression and performance statistics

The accuracy and reliability of the measured data sets to be used in regression of model parameters is an important issue related to modelling of phase equilibria. It is clear that good parameters for any model cannot be obtained from low quality data. Also due to systematic errors present in experimental data, VLE data sets do not satisfy exactly the Gibb-Duhem equation. Hence, the deviation between the experimental and calculated data by a chosen thermodynamic model can quantify the quality of the data set, once verified that the thermodynamic model can represent the class of compounds present in the analyzed system. In the case of the thermodynamic models, an objective function that considers the measurement uncertainties would be desirable when the experimental data contain random or systematic errors. In this work, the performance of thermodynamic models using different approaches for the objective function was analyzed. First, the objective function that considers least squares (LS) and another that considers the maximum likelihood estimation (MLE) are compared using representative experimental data sets. Also, the thermodynamic model performance using measured values of temperature, liquid mole fraction, or activity coefficients was analyzed.

Least Squares (LS) approach

For the regression of thermodynamic model parameters, the method of least squares is commonly employed. In this method, the minimization of sum of the squares of the errors between the experimentally measured values and the calculated values using the model provides the values of unknown model parameters and is given by,

$$\Delta A = \sqrt{\sum_{i}^{NC} \frac{(X_i - \hat{X}_i)^2}{NC}}, \qquad \text{for } i = 1,\ NC \tag{11}$$

where X_i is the experimental temperature, solute liquid mole fraction, or activity coefficient depending on the selected objective function, $\hat{X}_i$ is the calculated value of

the variable X_i for each compound i using a thermodynamic model, and NC is the total number of the compounds used in the parameter regression.

Maximum Likelihood Estimation (MLE) approach

The derivative of the probability density function of the measurement errors is considered in the Maximum Likelihood Estimation (MLE) method. For VLE systems, different authors (e.g., Fabries and Renon [182], Anderson et al.[183], and Kemeny et al.[184]) report improved results considering the MLE approach.

The fundamental concept is that when measurement errors follow a Gaussian distribution, the MLE objective function can be written as:

$$MLE = -\sum_{i=1}^{N}\left[\frac{1}{2}\ln(2\pi)+\ln(\sigma_i)+\frac{1}{2\sigma_i^2}\left(X_i-\hat{X}_i\right)^2\right] \tag{12}$$

where N is the number of the observations of different quantities, σ_i is the estimated standard deviation of measurement uncertainty, X_i is the experimental temperature, solute liquid mole fraction, or activity coefficient depending on the selected objective function and $\hat{X}_i$ is the calculated value of the variable X_i. The negative sign of the function is just used while considering the maximization of the objective function.

Property estimation considering different objective functions

To compare the performance of the various thermodynamic models using different objective functions, two SLE systems with high quality factors were chosen from the CAPEC_Lipids_Mixtures_Database. The following equations are used:

$$\mathrm{ARD}_{\%T} = \frac{100}{N}\sum_{\mathrm{i}}^{\mathrm{N}}\frac{\left|T_{\mathrm{i}}^{\mathrm{exp}}-T_{\mathrm{i}}^{\mathrm{calc}}\right|}{T_{\mathrm{i}}^{\mathrm{exp}}}, \qquad \text{for i} = 1,\ \mathrm{N} \tag{13}$$

$$\mathrm{ARD}_{x_1} = \frac{100}{N}\sum_{\mathrm{i=1}}^{\mathrm{N}}\left|x_{1\mathrm{i}}^{\mathrm{exp}}-x_{1\mathrm{i}}^{\mathrm{calc}}\right|, \text{ for i} = 1,\ \mathrm{N} \tag{14}$$

$$\mathrm{ARD}_{\gamma_1} = \frac{100}{N}\sum_{\mathrm{i=1}}^{\mathrm{N}}\left|\gamma_{1\mathrm{i}}^{\mathrm{exp}}-\gamma_{1\mathrm{i}}^{\mathrm{calc}}\right|, \qquad \text{for i} = 1,\ \mathrm{N} \tag{15}$$

Where $T_{\mathrm{i}}^{\mathrm{exp}}$ is the measured temperature, $x_{1\mathrm{i}}^{\mathrm{exp}}$ is the measured mole fraction, $\gamma_{1\mathrm{i}}^{\mathrm{exp}}$ is the experimental activity coefficient, calculated by $\gamma_{1\mathrm{i}}^{\mathrm{exp}} = \frac{y_{1\mathrm{i}}^{\mathrm{exp}}P}{P_{1i}^{sat}x_{1\mathrm{i}}^{\mathrm{exp}}}$; and $T_{\mathrm{i}}^{\mathrm{calc}}$, $x_{1\mathrm{i}}^{\mathrm{calc}}$ and $\gamma_{1\mathrm{i}}^{\mathrm{calc}}$

are the temperature, mole fraction, and activity coefficient values calculated from the model at each of the N data points, respectively. Note that values of $AAD_{\%T}$ are usually smaller than those of AAD_{x_i} since the former is a relative term while the latter is an absolute term; comparisons of the different ARD values should not be made.

To compare the performance of the well-known thermodynamic models (NRTL, UNIQUAC and UNIFAC) using the different objective functions, two SLE systems with high quality factors were chosen from the CAPEC_Lipids_Mixtures_Database. The results are given in Table 9 and 10. The objective function of Eq. (12) with the deviations of Eq. (13) is labelled MLE_T, while that with the deviations of Eq. (14) is labelled MLE_x and that with the deviations of Eq. (15) is labelled MLEγ. Models with regressed parameters are NRTL, UNIQUAC, original UNIFAC and FST (Eq. 3-5). The ARD values are from Eq. (13) for MLE_T, from Eq. (14) for MLE_x and from Eq. (15) for MLEγ. The parameters from NRTL are g_{12}-g_{22} (J/mol) and g_{21}-g_{11} (J/mol), plus α_{12}. The parameters from UNIQUAC are u_{12}-u_{22} (J/mol) and u_{21}-u_{11} (J/mol). The parameters from the FST model are a, b, and c, respectively. Calculations were done for comparison with group parameters from the Original UNIFAC parameters.

It can be seen that the well-known thermodynamic models such as NRTL, UNIQUAC and UNIFAC give only slightly different ARD values, with the FST model regression giving the lowest ARD and the original UNIFAC giving the highest, though the values are reasonably good. Note that the parameter values from the different objective functions are also similar. This is consistent with results shown in our previous results on lipid VLE data.

Table 9. SLE model performance for lipid systems from Test 2 with different objective functions. Experimental data: lauric acid(1) + myristic acid(2) for P = 101.3KPa and temperature from 316.94 – 327.48K [177].

Objective Function (Model)[a]	ARD[a]	Parameters[a]		
MLE_T (NRTL)	0.197	-868.52	-970.49	0.3
MLE_x (NRTL)	2.736	-864.57	-864.16	0.3
MLE_γ (NRTL)	$0.118_{(T)}$ and $1.235_{(x)}$	-925.16	-924.67	0.3
MLE_T(UNIQUAC)	0.194	-110.41	-110.36	-
MLE_x (UNIQUAC)	2.795	-101.09	-101.03	-
MLE_γ (UNIQUAC)	$0.137_{(T)}$ and $1.455_{(x)}$	-110.11	-110.03	-
MLE_T (FST)	0.086	4.61	-1490.04	-0.98
MLE_x (FST)	0.804	4.58	-1482.22	-0.01
MLE_γ (FST)	$0.094_{(T)}$ and $0.796_{(x)}$	4.59	-1484.04	-1E-05
MLE_T (Orig. UNIFAC)	0.505	-	-	-
MLE_x (Orig. UNIFAC)	5.478	-	-	-

[a] See text for definitions

Table 10. SLE Model performance for lipid systems from Test 2 with different objective functions. Experimental data: myristic acid(1) + stearic acid(2) for P = 101.3KPa and temperature from 328.88 – 343.98 K [181].

Objective Function (Model)[a]	ARD[a]	Parameters[a]		
MLE_T (NRTL)	0.321	-452.44	-452.28	0.3
MLE_x (NRTL)	4.399	-332.24	-332.17	0.3
MLE_γ (NRTL)	$0.197_{(T)}$ and $2.133_{(x)}$	-2867.51	2594.27	0.3
MLE_T(UNIQUAC)	0.333	-40.22	-40.22	-
MLE_x (UNIQUAC)	4.53	-26.30	-26.33	-
MLE_γ (UNIQUAC)	$0.269_{(T)}$ and $2.555_{(x)}$	-92.36	-92.32	-
MLE_T (FST)	0.248	2.68	-904.00	-0.79
MLE_x (FST)	1.418	3.32	-1120.27	-0.31
MLE_γ (FST)	$0.162_{(T)}$ and $1.555_{(x)}$	4.09	-1378.30	-0.01
MLE_T (Orig. UNIFAC)	0.409	-	-	-
MLE_x (Orig. UNIFAC)	4.823	-	-	-

[a] See text for definitions

Since the original UNIFAC model parameters may not have been regressed with data from lipid systems, a possible way to improve the original UNIFAC performance is to fine-tune group interaction parameters using the lipid SLE data-sets with their quality factors. This was done by regressing the interaction parameters for the functional group conected with a chain group, such as COOH with the CH3/CH2 group for fatty acids. There was some lowering of the ARD which was independent of the form of the objective function. Table 11 and 12 lists these UNIFAC results for the systems of Table 9 and 10.

Table 11. UNIFAC model performance for lipid systems from regression of group interaction parameters. Experimental data: lauric acid (1) + myristic acid(2) for P = 101.3 KPa and temperature from 316.94 – 327.48 K [177].

Objective Function (Model)[a]	ARD[a]	Parameters[a]	
MLE_T (Modified UNIFAC)	0.459	-2644.38	-5302.61
MLE_x (Modified UNIFAC)	4.989	-5892.38	-7317.22
MLE_γ (Modified UNIFAC)	$0.456_{(T)}$ and $4.322_{(x)}$	-7516.11	-7614.68

[a] See text for definitions

Table 12. UNIFAC model performance for lipid systems from regression of group interaction parameters. Experimental data: myristic acid(1) + stearic acid(2) for P = 101.3KPa and temperature from 328.88 – 343.98 K [181].

Objective Function (Model)[a]	ARD[a]	Parameters[a]	
MLE_T (Modified UNIFAC)	0.330	-9093.35	-3536.50
MLE_x (Modified UNIFAC)	4.477	-7377.00	-1169.82
MLE_γ (Modified UNIFAC)	$0.220_{(T)}$ and $2.409_{(x)}$	-53521.76	-4705.490

[a] See text for definitions

4.1.3 Uncertainty analysis of thermodynamic models

To estimate the uncertainty of the predicted temperature or molar fractions calculated using the thermodynamic models (NRTL, UNIQUAC, UNIFAC, FST), the information of the covariance COV(P*) of the parameters, and the local sensitivity J(P*) of the thermodynamic models has been used. For non-linear models, such as the thermodynamic models, the local sensitivities are obtained by differentiating the property model with respect to the estimated final model parameters. To calculate 95% confidence intervals of the predicted temperature or molar fraction, the covariance matrix COV(P*) and the local sensitivity J(P*) are substituted in the equation 16.

$$\hat{A}_i = \hat{A}_i \pm \sqrt{diag\left(J(\mathbf{P}^*)COV(\mathbf{P}^*)J(\mathbf{P}^*)^T\right)}t\left(\nu, \alpha_t/2\right) \quad (16)$$

where $\hat{A}_i$ is the calculated value of the variable A_i (Temperature or Molar fraction). For 95% confidence interval, the t-distribution value correspond to 0.05/2 percentile (i.e. $\alpha_t/2$ percentile).The covariance matrix of the parameters is given in Table 13 for the lipid examples.

Table 13. Covariance matrix $COV(\mathbf{P}^*)$ for thermodynamic models parameters.

Objective Function (Model)[a]	Covariance matrix $COV(\mathbf{P}^*)$					
	System A[177]			System B[181]		
MLE_T (NRTL)	85.964	-	-	565.207	-	-
	-59.415	41.201	-	-527.002	491.856	-
MLE_x (NRTL)	256.108	-	-	2.383	-	-
	-200.420	157.502	-	-2.253	2.132	-
MLE_T(UNIQUAC)	1.450	-	-	2.833	-	-
	-1.386	1.325	-	-2.812	2.791	-
MLE_x (UNIQUAC)	5.933	-	-	1.709	-	-
	-5.681	5.441	-	-1.697	1.685	-
MLE_T(UNIFAC)	0.020	-	-	0.052	-	-
	-0.191	1.838	-	-0.677	8.861	-
MLE_x (UNIFAC)	0.098	-	-	0.006	-	-
	-0.949	9.217	-	-0.080	1.043	-
MLE_T (FST)	6.073	-	-	6.604	-	-
	0.333	0.018	-	1.089	0.180	-
	-0.180	-0.010	0.005	-0.349	-0.058	0.019
MLE_x (FST)	9.040	-	-	2.298	-	-
	3.914	1.703	-	-0.472	0.097	-
	-5.273	-2.248	3.232	0.113	-0.023	0.006

[a] See text for definitions

In Table 13 only lower triangular matrix elements are given since the upper triangular matrix elements are identical. For non-linear models, such as thermodynamic models, the local sensitivities are obtained by differentiating the property model with respect to the estimated final model parameters. To calculate 95% confidence intervals of the predicted temperature or molar fraction, the covariance matrix COV(P*) and the local sensitivity J(P*) are substituted in the equation (16). The results of the uncertainty analysis for the different models can be seen in Figure 15 for the experimental data (System B). The thermodynamic models considered in the uncertainty analysis were

NRTL, UNIQUAC, UNIFAC and FST, identified above each diagram present in the Figure 15 by MLE(NRTL), MLE(UNIQUAC), MLE(UNIFAC) and MLE(FST).

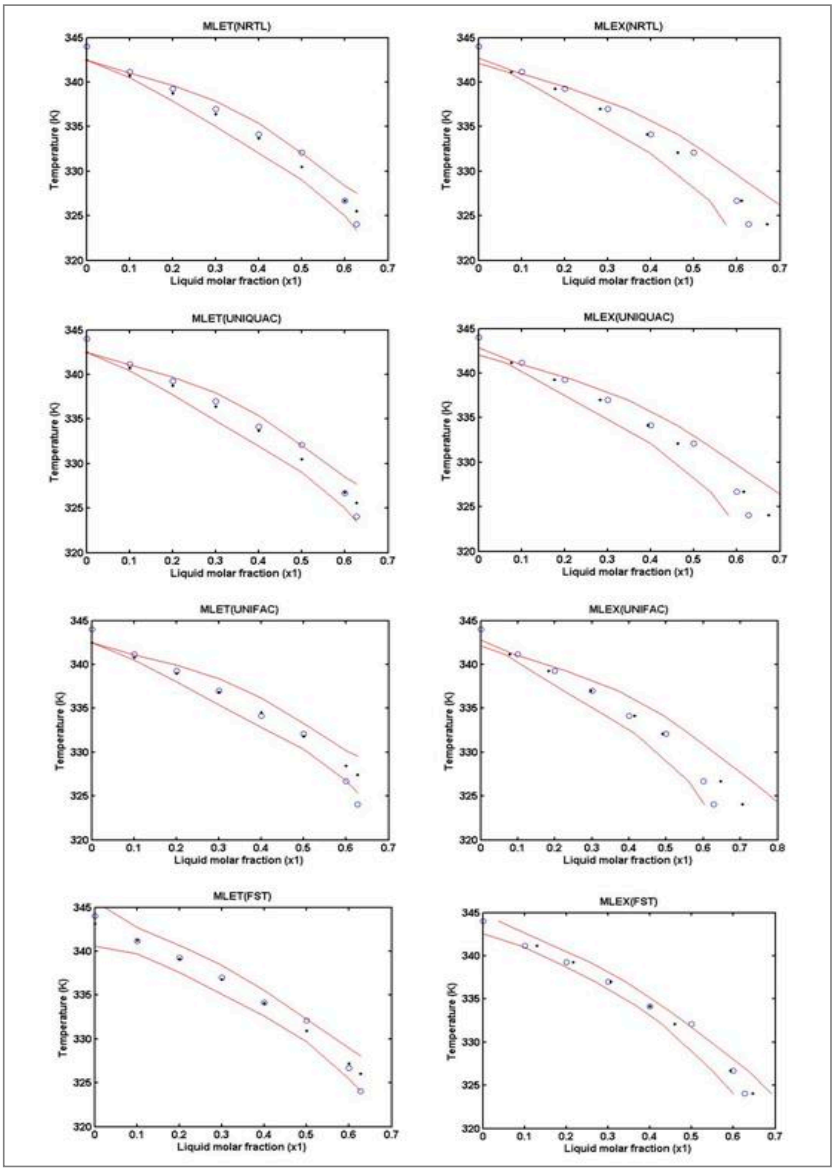

Figure 15: Uncertainty analysis: myristic acid(1) + stearic acid(2) SLE ○Experimental data [181] ; •Thermodynamic models; — ±95% confidence interval calculated using equation (16).

Since System A (Tables 9 and 11) showed same behaviour as System B (Tables 10 and 12), only the results for the System B are presented. For NRTL and UNIQUAC models, the pure component properties (melting point and enthalpy of fusion) determine the behaviour of the model at the end points, while the model parameters affect the intermediate points. Nevertheless, the FST model shows similar behaviour for both molar fraction and temperature calculations, and similar dependence of the model parameters for all the experimental points of the system. It is also important to highlight that for the FST model all the points are included in the 95% confidence interval calculated by equation (16).

4.1.4 Influence of pure component properties in thermodynamic calculations

The uncertainty analysis of the parameter estimation for well-known thermodynamic models (NRTL, UNIQUAC and original UNIFAC) and SLE systems have confirmed the importance of the pure component properties. For VLE, vapour pressure coefficients play an important role in the phase diagram calculation for symmetric well-know thermodynamic models such as NRTL, UNIQUAC and original UNIFAC. The problem was also pointed by Kang et al. [131] in the analyze of available VLE data considering different thermodynamic consistency tests. For lipids, it was observed that same values of vapour pressure coefficients could not be used accurately for all the data sets containing the same pure component. The cited problem is illustrated in Figure 16 for chosen mixtures containing decanoic acid as one of the compounds. In Figure 16, Müller and Stage [185] has measured different VLE data sets containing lipids and many of them show good agreement for the pure component information of boiling point in item a) and b). However, in item c) of Figure 16, the boiling point of decanoic acid present high deviation utilizing the same thermodynamic model (original UNIFAC) and vapour pressure coefficients for the decanoic acid.

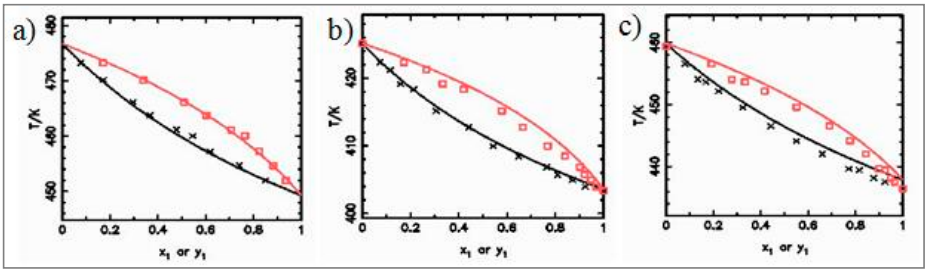

Figure 16: Data sets containing decanoic acid as one of the compounds. a) Octanoic acid + dodecanoic acid at 2.7KPa; b) Decanoic acid + dodecanoic acid at 0.5KPa; c) Decanoic acid + dodecanoic acid at 2.7KPa. Experimental data [185]: liquid phase (x) and vapour phase (□). Original UNIFAC model prediction of liquid phase (—) and vapour phase (—).

For SLE, mixtures including triolein [178,186,187] were considered as an example, values reported for the melting point can be seen in Table 14.

Table 14: Melting point values observed in literature for triolein

Melting point (K)	References
278.7	Nishimura et al. [187]
279.22	Costa et al. [186]
278.43	Rolemberg et al. [178]

Comparing the available values of melting point in literature showed in Table 14 with the solid solubility data of triolein in acetone gave by Privett and Boyer [188], have demonstrated that there is a disagreement between the values reported by the authors, as can be seen in Figure 17.

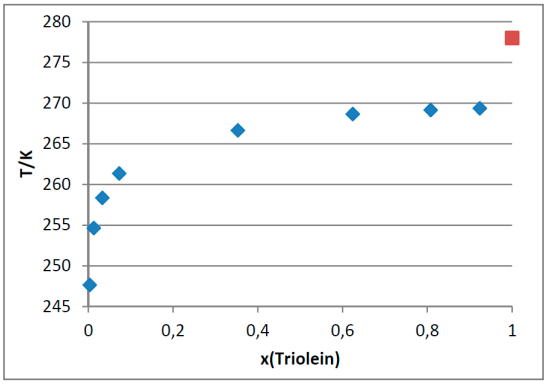

Figure 17: Disagreement found for SLE data. ◆Experimental data of triolein solid solubility in acetone by Privett and Boyer [188] and ■Triolein melting point by Rolemberg et al. [178].

4.2 Original UNIFAC model improvement for lipids systems

Since the original UNIFAC model parameters may not have been regressed with data from lipid systems, a possible way to improve the original UNIFAC performance is to fine-tune the group interaction parameters using the lipid SLE data-sets with their quality factors. This was done by regressing the interaction parameters for the functional group with the chain group, such as COOH with the CH3/CH2 group for fatty acids. The groups used for original and modified UNIFAC parameter regression are presented in Table 15. In Table 15, X indicates groups that can be found for the original UNIFAC table; Y means a gap in the original UNIFAC group table while first-order group parameters of the KT-UNIFAC [189] are available; and + means the group parameters do not exist in either original or KT-UNIFAC [189] models.

In order to improve the performance of predictive thermodynamic models for lipids data, a detailed analysis of the original UNIFAC model was performed and a new set of interaction parameters for UNIFAC model and lipids systems were proposed.

Table 15: UNIFAC groups for lipids.

Compounds	CH3	CH2	CH	CH=CH	CH=C	C=C	ACH	AC	AC-CH3	CH2 cyc	CH cyc	C cyc	CH=C cyc	C=C cyc	OH	AC-OH	CH3COO	CH2COO	CH-O	O cyc	CH2NH2	COOH	PHO4	P=0	O^-
Fatty Acids (FA)	X	X		X																		X			
Methyl Esters (ME)	X	X		X													X								
Ethyl Esters (EE)	X	X		X														X							
Triacylglycerols (TAGS)	X	X	X	X														X							
Diacylglycerols (DAGS)	X	X	X	X											X			X							
Monocylglycerols (MAGS)	X	X	X	X											X			X							
Phospholipids	X	X	X	X											X			X	X		X		+	+	+
Tocopherols	X	X	X				X	X	X	Y		Y				X				Y					
Tocotrienol	X	X					X	X	X	Y		Y				X				Y					
Carotenes	X			X	X	X					Y	Y	Y	Y											
Lutein	X			X	X	X					Y	Y		Y	X										
Lycopene	X	X		X	X							Y													
Squalene	X	X			X																				
Zeaxanthin	X		X	X	X	X					Y			Y	X										
Campesterol	X	X	X								Y	Y	Y		X										
Cholesterol	X	X	X								Y	Y	Y		X										
Sitosterol	X	X	X								Y	Y	Y		X										
Stigmasterols	X	X	X	X							Y	Y	Y		X			X							
Sterol Glycosides	X	X	X	X	X						Y	Y	Y		X			X		Y					+

4.2.1 Regularization term utilized in original UNIFAC model for parameter regression

Since a large number of interaction parameters were necessary for the VLE calculation compared with the measured data points an objective function employing a regularization term [190] F_R was considered:

$$F_{UNIFAC} = F_{VLE} + F_R \tag{17}$$

$$F_R = \frac{1}{\beta}\sum_m \sum_n \left(a_{mn} - a_{mn}^0\right)^2 \tag{18}$$

This was also done by Balslev and Abildskov [191]. Considering this objective function (Eq. (17)), only the most sensitive parameters are allowed to deviate from their nominal values, a_0. The value of β is empirical. It is determined from several minimizations monitoring the parameter norm, βFR, and the residual norm, FVLE. When β is small (i.e. 10^3), the residual norm is great. Then by increasing β the parameter norm will increase and the residual norm decreases up to some optimal value of β (typically 10^4 or 10^5), after which the residual norm no longer decreases, but the parameter norm continues to increase.

Differences in accuracy can be found for original UNIFAC model in comparison with correlated models such as NRTL and UNIQUAC, though they are not large for some of the systems, as showed before. For original UNIFAC model, 52 VLE data sets in total including 632 data points were considered in parameter regression of 48 binary interaction parameters (a_{mn}). Some of the data sets available for VLE and lipids were not considered in the parameter regression due to data consistency problems. Also the experimental data sets containing pseudo compounds, as vegetable oils and biodiesel, were not considered in the parameter regression once the composition of pseudo-compounds is estimated in some cases. Mixtures containing glycerol were also not considered in the regression once UNIFAC model has shown good model representation of the compounds. For the cases where inconsistency of the data was observed, such as inaccuracy of boiling point (Figure 18) or high measurement uncertainty, as shown in Figure 19 below, the data sets were also not considered in the parameter regression. The residual between the experimental data and the model calculation is considered in the regularization term and can result in inclusion of such uncertainties in the final values of

model parameters. In total 17 data sets were not be included in the parameter regression due the cited problems.

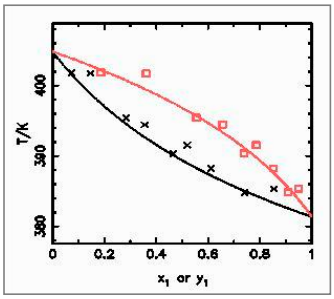

Figure 18: Octanoic acid + Dodecanoic acid at 0.5KPa. Experimental data [185]: liquid phase (x) and vapour phase (□). Original UNIFAC model prediction of liquid phase (—) and vapour phase (—).

The considered data sets include different types of compound combinations in the mixture (fatty acid and fatty ester, fatty ester and alcohol, monoacylglycerol and fatty ester, monoacylglycerol and fatty acid, fatty acid and alcohol, fatty acid and alkane, triacylglycerol and acetone and triacylglycerol and alkane). The group contribution parameters considered for original UNIFAC model after the parameter regression are listed in Table 16 below.

Table 16: UNIFAC parameters regressed considering lipids data.

Groups	CH3/CH2	CH=CH	OH	CH3OH	CH3CO	CH2COO	COOH	OH(acy)
CH3/CH2	0	301.91	630.11	635.3	462.3	851.78	601.82	689.2
CH=CH	1257.3	0	777.38	908.12	146.35	233.52	-6502	-
OH	167.84	-509.05	0	-137.1	84	315.25	199	-
CH3OH	60.71	-268.19	249.1	0	23.39	192.93	237.12	-
CH3CO	157.45	-505.79	164.5	108.7	0	259.15	669.4	-
CH2COO	998.03	-952.86	556.44	418.54	333.14	0	521.21	666.28
COOH	1195.86	-451.67	-151	-108.18	-297.8	-240.75	0	-219.26
OH(acy)	364.76	-	-	-	-	-763.15	-615.56	0

The inclusion of an additional group for monoacylglycerol (OH acyl) has showed good improvement in the original UNIFAC model representation for the systems containing these compounds. This improvement is observed in both pressures (1.2 KPa and

2.5KPa) and is shown in Figure 19 and 20 for the binary mixture containing monoacylglycerol. The binary interaction parameter matrix also brings the gaps found for experimental data. The combination between monoacylglycerols or diacylglycerols with unsaturated compounds, alcohols and acetone are still missing in literature.

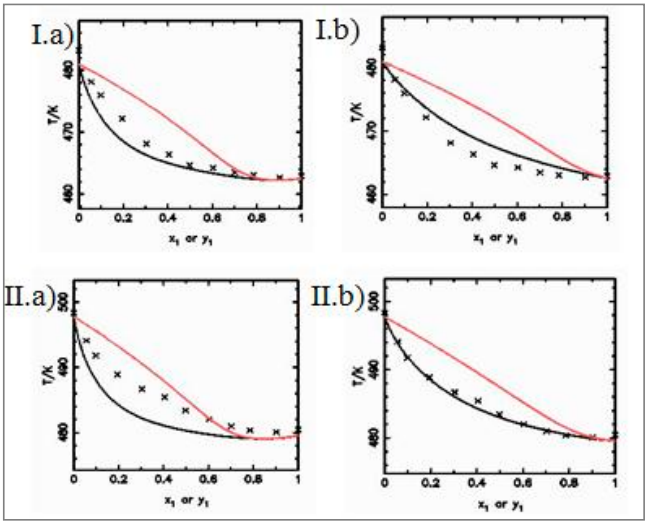

Figure 19: Monocaprylin(1) and palmitic acid (2) – original UNIFAC model representation a) before and b) after consider the new set of parameters. I) Pressure: 1.2KPa, II) Pressure: 2.5KPa. Experimental data (this work): liquid phase (x). Original UNIFAC model prediction of liquid phase (—) and vapour phase (—).

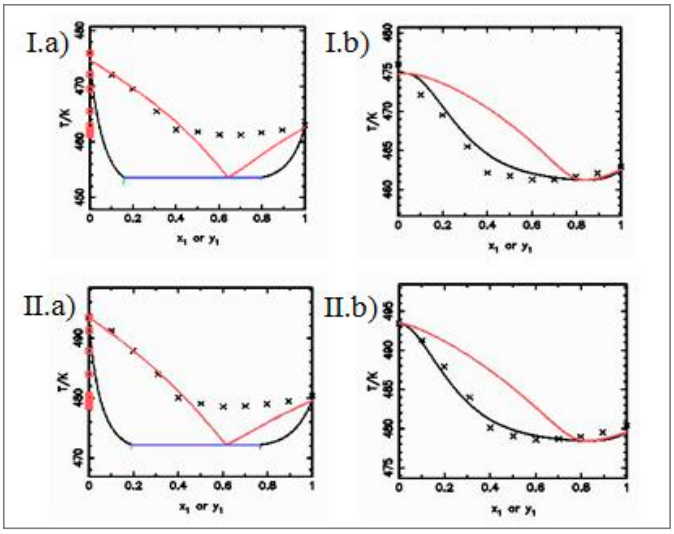

Figure 20: Monocaprylin(1) and methyl stearate(2) – original UNIFAC model representation a) before and b) after consider the new set of parameters. I) Pressure: 1.2KPa, II) Pressure: 2.5KPa. Experimental data (this work): liquid phase (x). Original UNIFAC model prediction of liquid phase (—) and vapour phase (—).

The experimental data containing monoacylglycerol and presented in Figure 19 and 20 are part of the experimental work developed in this project and has more details descried in Chapter 7 – Experimental work procedure.

It was observed that original UNIFAC model predicted unrealistic two liquid phases for the systems containing monocaprylin and methyl stearate (Figure 20). The same was observed for example by Orbey et al. [192] for the system containing 2-propanol and water, and was reported by Kanda et al. [14], where UNIFAC-Dortmund have predicted unreal LLE split for systems containing ethyl palmitate and ethanol. Unreal LLE split was also observed for data set considered in the parameters regression containing methyl oleate and methanol, as can be seen in Figure 21 below.

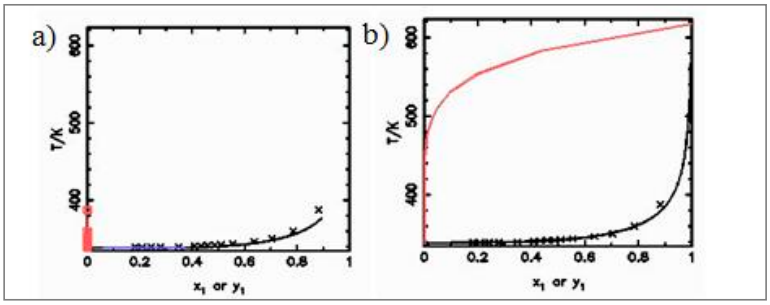

Figure 21: Methyl oleate (1) and methanol (2) – original UNIFAC model representation a) before and b) after consider the new set of parameters. Experimental data [193]: liquid phase (x). Original UNIFAC model prediction of liquid phase (—) and vapour phase (—).

Regarding mixtures containing methyl ester and alcohol, it was observed that original UNIFAC model have the tendency to show negative deviation with the experimental data, what can be seen in Figure 22. Improvement in model representation for original UNIFAC model was found after considering the new set of parameters given in Table 11. Improvement was also observed in the data set containing a mixture of a fatty acid and fatty ester (lauric acid and methyl laurate), as can be seen in Figure 23 below.

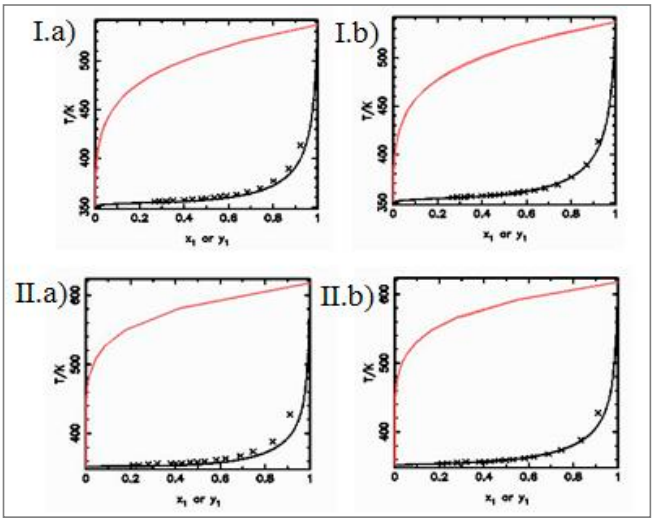

Figure 22: I) Methyl laurate (1) and ethanol (2) and II) Methyl oleate (1) and ethanol (2) – original UNIFAC model representation a) before and b) after consider the new set of parameters. Experimental data [193]: liquid phase (x). Original UNIFAC model prediction of liquid phase (—) and vapour phase (—).

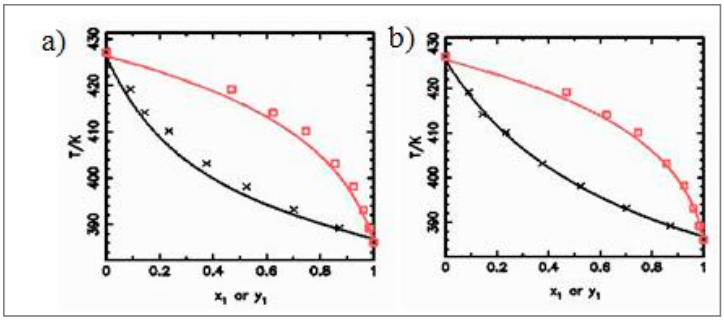

Figure 23: Lauric acid (1) and methyl laurate (2) – original UNIFAC model representation a) before and b) after consider the new set of parameters. Experimental data [176]: liquid phase (x) and vapour phase (□). Original UNIFAC model prediction of liquid phase (—) and vapour phase (—).

For more non-ideal systems, as the ones containing solvents such as hexane and acetone, high deviation were observed for original UNIFAC model as can be seen in Figures 24 and 25. Significant improvement was observed after the new set of parameters was introducted.

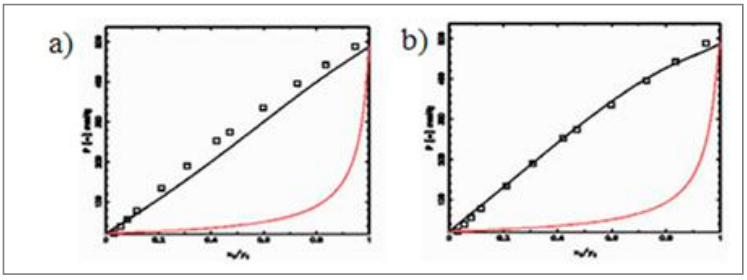

Figure 24: Hexane (1) and oleic acid – original UNIFAC model representation a) before and b) after consider the new set of parameters. Experimental data [194]: liquid phase (x). Original UNIFAC model prediction of liquid phase (—) and vapour phase (—).

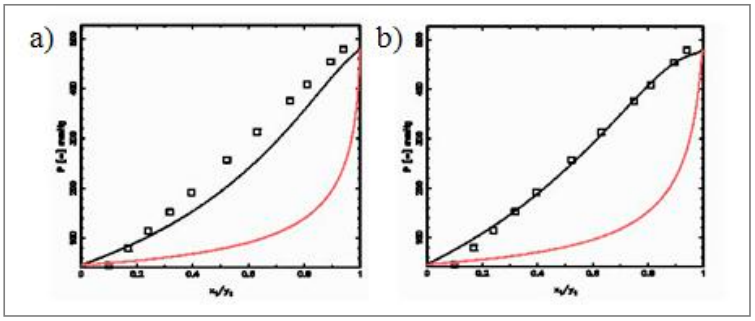

Figure 25: I) Acetone (1) and triolein (2) – original UNIFAC model representation a) before and b) after consider the new set of parameters. Experimental data [194]: liquid phase (x). Original UNIFAC model prediction of liquid phase (—) and vapour phase (—).

To better visualize the performance of the new set of parameter in the calculation of VLE and SLE data sets considering original UNIFAC, Figure 26 and 27 bring the experimental versus the calculated temperature (K). It is possible to observe good agreement between original UNIFAC prediction for VLE data sets including lipids, but the results observed for SLE data sets present more deviation. Considering the melting point data as a function of composition exist and the disagreement observed for in different data sets including the same compound, as showed in Figure 17, it is possible to conclude that there is not much to be gained including SLE data in the analysis.

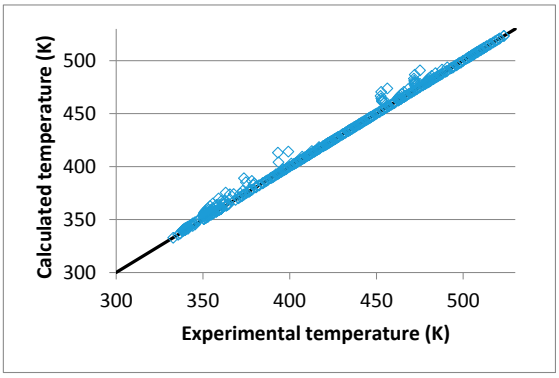

Figure 26: Experimental temperature considering all VLE data sets versus calculated temperature utilizing original UNIFAC model and the new set of the proposed parameters (Table 11).

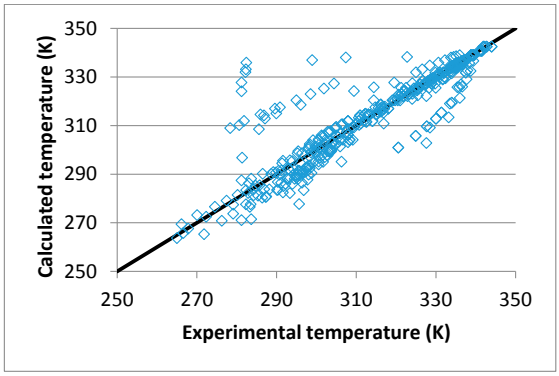

Figure 27: Experimental temperature considering all SLE data sets versus calculated temperature utilizing original UNIFAC model and the new set of the proposed parameters (Table 11).

4.2.2 Cross-validation of the regressed parameters

Aiming to analyze the parameters obtained, experimental data for VLE systems containing lipids were divided randomly into 5 different groups (A, B, C, D and E) and parameter regression for original UNIFAC model was performed considering the exclusion of one group each time. The ARD(%) found for each variation of combined groups considering the regressed parameters (Table 16) and lipids systems are given in Table 17. For the calculation of ARD(%), equation 13 was used. The ARD(%) between the experimental and calculated temperature for each group is given in Table 18.

Table 17: ARD(%) for the cross-validation variations.

Variations	ARD(%)
Orig. UNIFAC model parameters	3.080
Orig. UNIFAC model with lipids parameters	1.512
Cross-validation - ABCD	1.624
Cross-validation - ABCE	3.283
Cross-validation - ABDE	2.076
Cross-validation - ACDE	1.575
Cross-validation - BCDE	1.568

Table 18: ARD(%) for the cross-validation groups.

Groups	Orig.UNIFAC model parameters	Orig. UNIFAC model with lipids parameters	Cross-validation parameters
	ARD(%)	ARD(%)	ARD(%)
A	0.573	0.142	0.329
B	0.202	0.176	0.511
C	1.782	1.387	3.611
D	9.190	2.310	11.145
E	3.600	3.359	3.927

It is possible to observe that the case where all the available data are considered, the ARD(%) obtained is lower than for original UNIFAC model parameters and for the cases considering cross-validation. Moreover, in the case of the group D, note that the division of the groups was random, the group for acetone, present one in one data set, was excluded of the parameter regression in the cross-validation. Thus, a high deviation is observed.

4.2.3 Original UNIFAC model representation of liquid solubility systems containing lipids

The original UNIFAC model parameters were compared with LLE parameters [12]. For data sets containing fatty acids and water, it is observed better model representation considering the LLE parameters, as can be seen in Figure 28. However, for data sets containing fatty esters, similar results are observed using original UNIFAC parameters and LLE parameters, as shown in Figures 29 and 30.

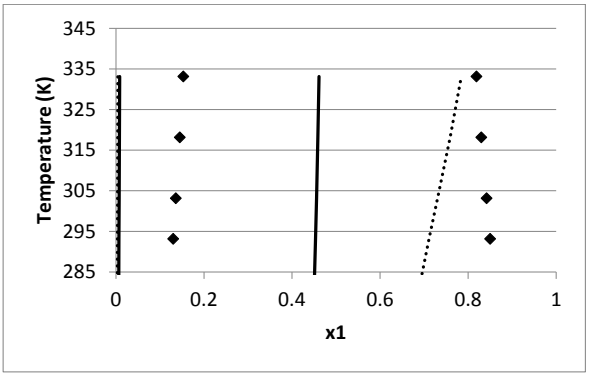

Figure 28: Hexanoic acid (1) and water (2). ◆Experimental data [195], (—) Original UNIFAC model prediction and (---) Original UNIFAC model prediction with LLE parameters.

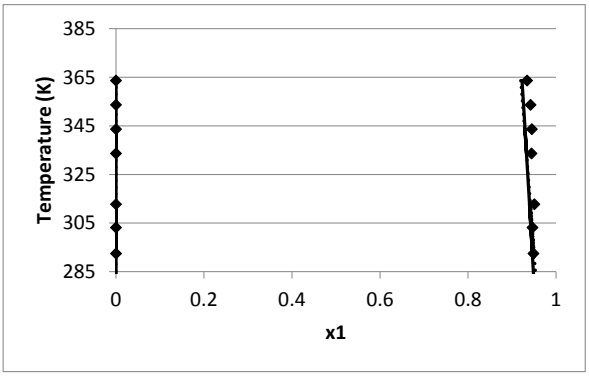

Figure 29: Methyl heptanoate (1) and water (2). ◆Experimental data [196], (—) Original UNIFAC model prediction and (---) Original UNIFAC model prediction with LLE parameters.

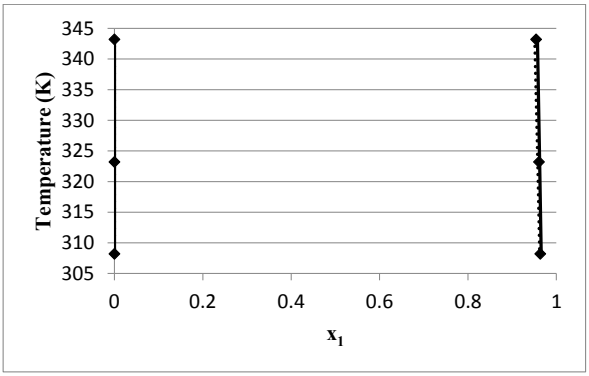

Figure 30: Methyl palmitate (1) and water (2). ◆Experimental data [197], (—) Original UNIFAC model prediction and (---) Original UNIFAC model prediction with LLE parameters.

The higher deviation observed between the experimental data and the calculated by UNIFAC model (both original and UNIFAC-LLE) for fatty acids can be explained by the fact of a necessity of term to take into account the association between the compounds. PC-SAFT model with association term could be an option to be tried.

4.3 Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) combined with GC methods

The purpose of this part of the project was the use of the combination of PC-SAFT equation with Group-Contribution (GC) method to describe associative compounds and their mixtures, present in lipids industry. The use of the cross-associating parameters is discussed in the calculation of physical properties of vapour pressure, enthalpy of Vapourization, density and heat capacity.

The PC-SAFT EoS can be expressed in the calculation of the compressibility factor as [43,44]:

$$Z = Z^{id} + Z^{hc} + Z^{disp} + Z^{assoc} \tag{19}$$

The complete set of equations utilized in this work is given in the work of Privat et al. [61] and the association term proposed by Gross and Sadowski [44] have been included:

$$Z^{assoc} = \rho \sum_i x_i \sum_j x_j \sum_{Ai} \left[\left(\frac{1}{X^{A_j}} - \frac{1}{2} \right) \frac{\partial X^{A_j}}{\partial \rho_i} \right] \tag{20}$$

$$\Delta^{A_iB_j} = \sigma_{ij}^3 g_{ij}\left(d_{ij}\right) \mathrm{K}^{A_iB_j}\left[exp\left(\frac{\varepsilon^{A_iB_j}}{kT}\right)-1\right] \quad (21)$$

PC-SAFT model considering the association term (Eq. 19-21) were compared with the same version of the model without the association term and considering the group-contribution (GC) method for the pure component parameters.

To use Group Contribution (GC) methods, it is necessary to assure that the parameters are linear functions of the group occurrences. For this analysis, the molecular weight of the compound was plotted versus the properties (pure component parameters). The parameter m_i that represents the number of segments per molecule has a linear function with the group occurrences. For σ_i (Å), that represents the diameter of a segment, Privat et al. [62] have found that $m_i.\sigma_i^3$ can be used as a linear function of the group occurrences. Finally, for ε_i / k (K), that is the energy parameter characterizing the dispersion forces was used by Privat et al. [62] as $m_i.\sigma_i.\varepsilon_i / k$ to obtain the linear function with the group occurrences. After the confirmation of the linear function with the group occurrences, the values of the groups could be regressed considering a classical group contribution equation [198] and the groups indicated by Ceriani et al. [169] for lipids systems:

$$f\left(X\right) = \sum_i N_i C_i + w\sum_j M_j D_j + z\sum_k O_k E_k \quad (22)$$

Where N_i is the occurrence of the first-order groups C_i, M_j is the occurrence of the second-order groups D_j, and O_k is the occurrence of the second-order groups E_k. For estimation in the first level, constants w and z are set to zero, while for second level, w is unit and z is equal zero, and finally for third level, all constants (w and z) are set to unity values. The function $f\left(X\right)$ is a target of the property X.

The first step in this part of the work was the analysis of the parameter values to guarantee the linear function of the group occurrences. The results found can be seen in Figure 31-34 for fatty acids (FA), methyl fatty esters (ME), ethyl fatty ester (EE) and triaclyglycerols (TAGS), respectively. It is important to notice here that only compounds with enough data for considered properties (vapour pressure, enthalpy of fusion and density) had the parameters regressed. In total, 54 different lipids were considered to fine-tune the pure component parameters for PC-SAFT model and lipids systems. The unsaturated compounds were identified in the graphics given by Figure

31-34 with a different mark colour and contain an additional group to represent the unsaturation.

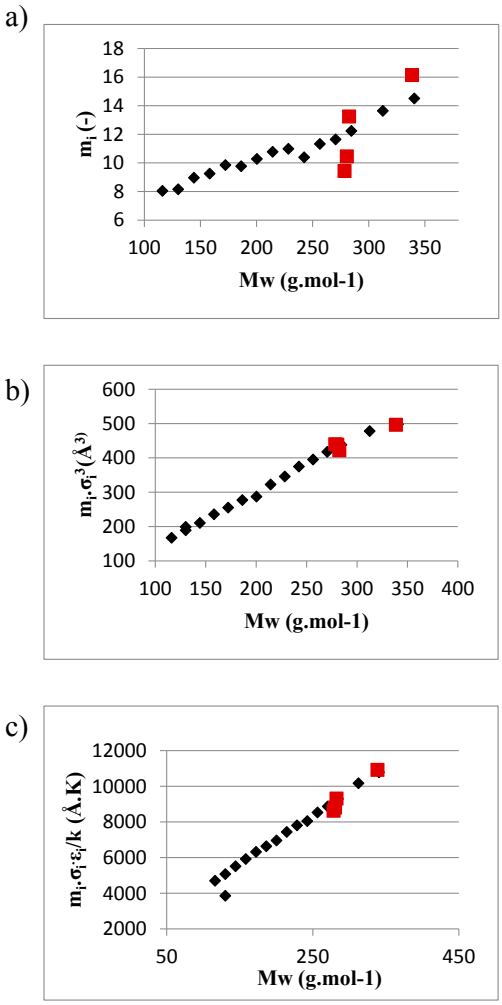

Figure 31: Linear function with the group occurrences for PC-SAFT model pure component parameters: a) m_i (-), b) $m_i.\sigma_i^3$ (Å^3) and c) $m_i.\sigma_i.\varepsilon_i / k$ (Å.K).◆Saturated FA and ■Unsaturated FA.

It is possible to observe that parameter m_i (-) values for ethyl esters are noisier in comparison with fatty acids and TAGS, as can be seen in Figure 33.

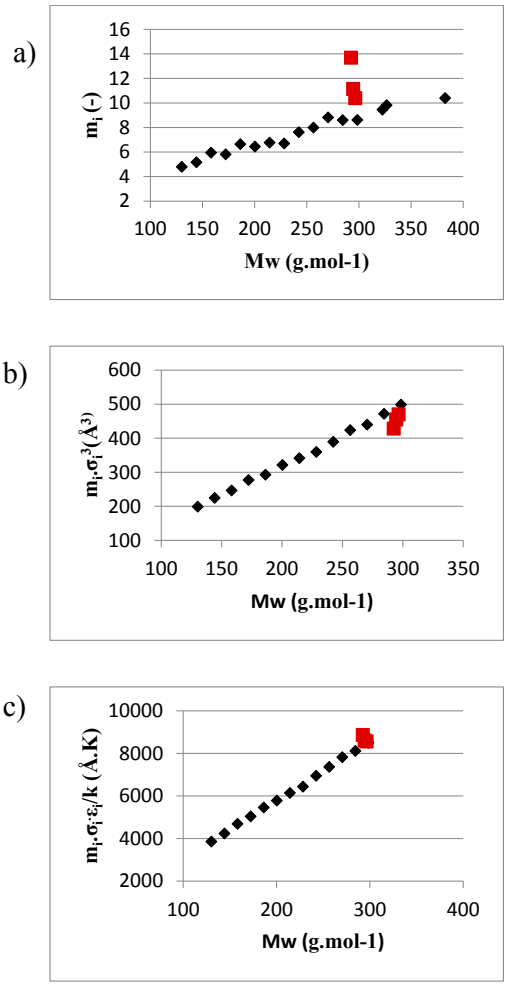

Figure 32: Linear function with the group occurrences for PC-SAFT model pure component parameters: a) m_i (-), b) $m_i.\sigma_i^3$ (Å^3) and c) $m_i.\sigma_i.\varepsilon_i / k$ (Å.K).◆Saturated ME and ■Unsaturated ME.

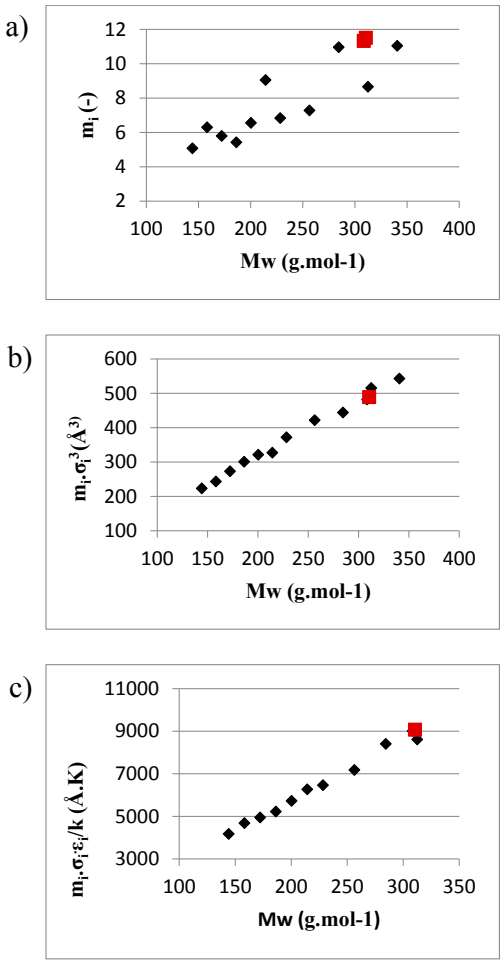

Figure 33: Linear function with the group occurrences for PC-SAFT model pure component parameters: a) m_i (-), b) $m_i.\sigma_i^3$ (Å^3) and c) $m_i.\sigma_i.\varepsilon_i / k$ (Å.K).◆Saturated EE and ■Unsaturated EE.

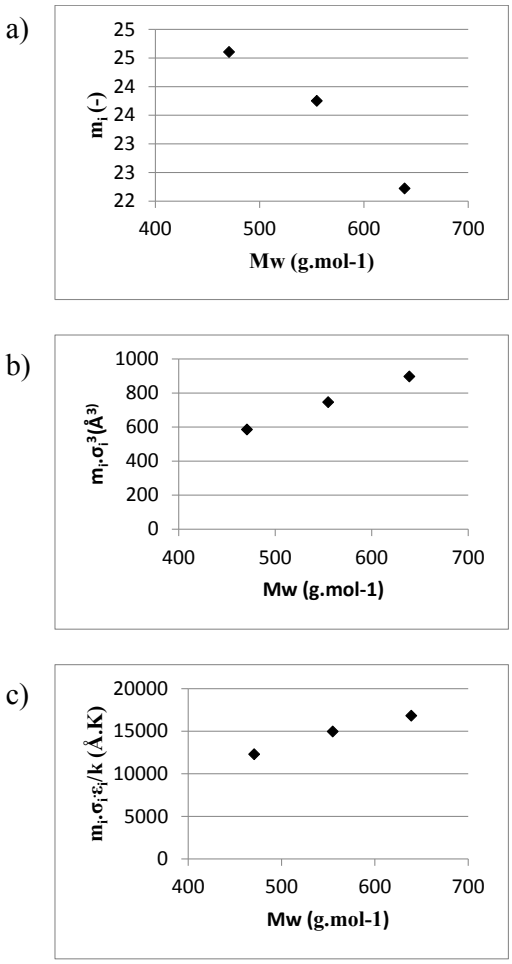

Figure 34: Linear function with the group occurrences for PC-SAFT model pure component parameters: a) m_i (-), b) $m_i.\sigma_i^3$ (Å^3) and c) $m_i.\sigma_i.\varepsilon_i / k$ (Å.K).◆Saturated TAGS.

After verification of the functional linearity of the parameters with the group occurrence, the groups were regressed considering the classical group contribution equation (Eq. 22). The values obtained for each group are given in Table 19 and the parameters values and deviations for the compounds considered in the regression (with enough experimental data for the necessary properties) can be seen in Table 20-23.

Table 19: Groups for PC-SAFT pure component parameters calculation.

Parameters	CH3	CH2	COOH	COO	CH=	CH2-CH-CH2
m_i (-)	78.933	0.366	-72.565	-154.589	0.593	195.000
$m_i.\sigma_i^3$ (Å^3)	114.641	24.498	-70.120	-131.899	18.689	246.496
$m_i.\sigma_i.\varepsilon_i / k$ (Å.K)	21460.408	404.671	-18650.938	-40762.799	237.159	63209.391

Table 20: Pure component parameters values for fatty acids.

Compounds	m_i (-)	σ_i (Å)	ε_i / k (K)	P^{sat} ARD(%)	Density ARD(%)	Enthalpy of vap. ARD(%)
Hexanoic acid	8.041	2.750	212.608	2.414	0.941	3.787
Heptanoic acid	8.153	2.852	218.295	4.821	0.704	8.407
Octanoic acid	8.960	2.864	214.873	4.332	0.720	0.844
Nonanoic acid	9.248	2.943	217.560	3.782	0.514	6.799
Decanoic acid	9.847	2.959	216.969	4.558	0.861	3.818
Undecanoic acid	9.766	3.050	222.825	4.879	1.808	1.610
Dodecanoic acid	10.274	3.035	223.247	4.993	2.105	13.211
Tridecanoic acid	10.773	3.105	222.403	6.468	1.640	4.774
Tetradecanoic acid	10.984	3.158	225.105	5.035	1.168	15.116
Pentadecanoic acid	10.389	3.304	234.514	3.717	1.089	5.099
Hexadecanoic acid	11.324	3.268	230.574	7.427	0.876	0.556
Heptadecanoic acid	11.641	3.298	231.076	1.936	1.056	1.495
Octadecanoic acid	12.235	3.296	230.568	6.425	1.483	13.928
Octadecenoic acid	13.243	3.171	221.747	11.517	3.003	13.321
Octadecadienoic acid	10.452	3.475	242.599	8.461	0.634	12.078
Octadecatrienoic acid	9.432	3.599	254.198	10.418	3.608	8.551
Eicosanoic acid	13.637	3.273	227.878	6.818	2.534	3.709
Docosanoic acid	14.505	3.250	228.817	9.922	7.917	2.000
Docosenoic acid	16.143	3.133	215.970	4.607	4.766	1.222

Table 21: Pure component parameters values for methyl esters.

Compounds	m_i (-)	σ_i (Å)	ε_i / k (K)	P^{sat} ARD(%)	Density ARD(%)	Enthalpy of vap. ARD(%)
Methyl hexanoate	4.791	3.463	232.568	2.423	3.508	1.900
Methyl heptanoate	5.165	3.517	233.363	3.357	2.727	2.411
Methyl octanoate	5.947	3.461	227.978	3.657	2.140	4.694
Methyl nonanoate	5.810	3.627	239.310	2.791	4.149	1.370
Methyl decanoate	6.641	3.533	232.829	3.227	1.242	4.156
Methyl undecanoate	6.446	3.681	243.824	1.810	1.869	0.750
Methyl laurate	6.768	3.695	245.711	4.034	0.377	0.378
Methyl tridecanoate	6.698	3.773	254.886	4.236	1.826	0.952
Methyl myristate	7.619	3.711	245.858	2.443	0.473	0.283
Methyl pentadecanoate	7.992	3.757	245.415	5.596	3.008	2.036
Methyl palmitate	8.821	3.681	241.002	6.881	1.490	1.842
Methyl heptadecanoate	8.602	3.799	248.470	3.073	2.473	1.241
Methyl stearate	8.618	3.868	254.966	14.048	2.420	4.081
Methyl oleate	10.392	3.563	231.331	8.417	0.618	2.389
Methyl linoleate	11.144	3.444	224.363	16.232	0.632	3.502
Methyl linolenate	13.691	3.151	205.601	21.711	1.762	9.144
Methyl eicosanoate	9.815	3.806	247.073	10.647	2.062	2.533
Methyl docosanoic	9.451	3.861	260.683	15.664	2.334	6.712
Methyl tetracosanoic	10.396	3.911	254.143	6.303	1.102	7.881

Table 22: Pure component parameters values for ethyl esters.

Compounds	m_i (-)	σ_i (Å)	ε_i / k (K)	P^{sat} ARD(%)	Density ARD(%)	Enthalpy of vap. ARD(%)
Ethyl hexanoate	5.074	3.531	232.943	2.768	1.786	1.427
Ethyl octanoate	5.793	3.613	236.380	1.724	0.855	7.505
Ethyl nonanoate	5.423	3.814	252.541	2.319	1.796	3.099
Ethyl decanoate	6.555	3.660	238.691	9.692	1.824	0.945
Ethyl laurate	6.835	3.790	249.556	5.090	1.600	0.380
Ethyl myristate	7.279	3.870	254.836	7.626	1.401	1.261
Ethyl stearate	8.657	3.905	254.768	12.271	0.582	11.892
Ethyl oleate	11.507	3.490	225.905	7.502	0.510	26.060
Ethyl linoleate	11.326	3.492	227.876	8.733	0.232	26.269

Table 23: Pure component parameters values for triacylglycerols.

Compounds	m_i (-)	σ_i (Å)	ε_i / k (K)	P^{sat} ARD(%)	Density ARD(%)	Enthalpy of vap. ARD(%)
Trioctanoin	24.605	2.877	173.733	12.731	6.199	18.747
Tridecanoin	23.751	3.156	199.689	30.745	5.605	26.921
Tridodecanoin	22.221	3.431	220.671	24.867	5.219	19.371

For TAGS it was observed a decrease in the values of parameter m_i (-) when increasing the carbon chair number, as given in Table 23. This was not observed before for other compounds, such as fatty acids and esters. To consider this effect, a constant was added in the TAGS calculation and Eq. 22 has the follow left-side:

$$\frac{X}{L} = \sum_i N_i C_i + w \sum_j M_j D_j + z \sum_k O_k E_k \tag{23}$$

Where X is the parameter value and L is a constant and equal a -1 for TAGS.

It was observed good agreement between the parameter and the calculated values from the regressed groups (Table 19). Figure 35-37 shows the parameter values versus the calculated considering the group contribution.

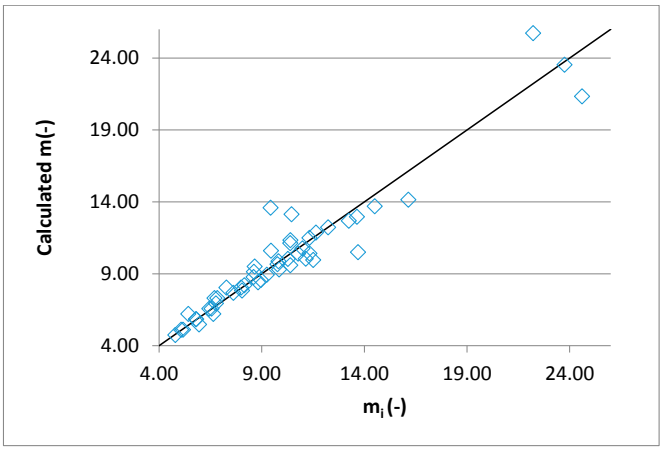

Figure 35: Values of parameter m_i (-) versus the calculated considering the group contribution (Table 19).

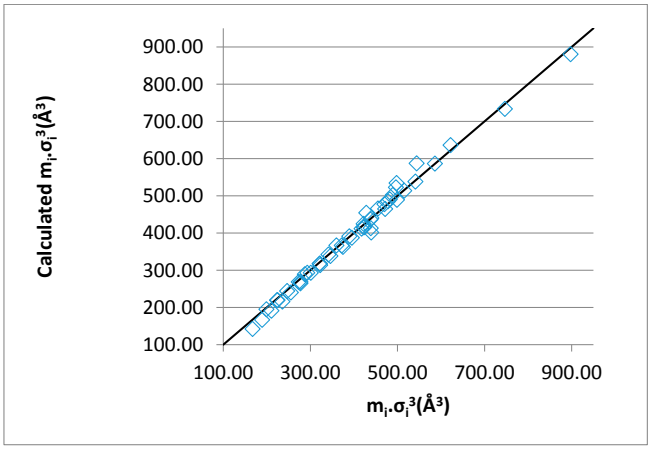

Figure 36: Values of parameter mi.σi^3(Å^3)
versus the calculated considering the group contribution (Table 19).

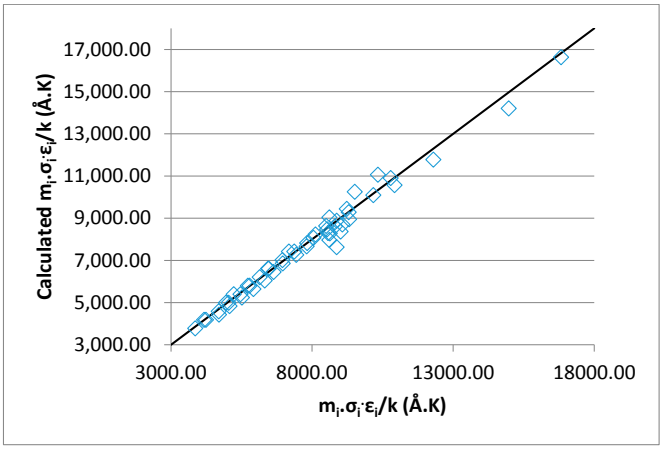

Figure 37: Values of parameter $m_i.\sigma_i.\varepsilon_i / k$ (Å.K) versus the calculated considering the group contribution (Table 19).

Two examples were selected to present the improvement of properties estimation (vapour pressure, enthalpy of fusion and density) considering PC-SAFT and GC after fine-tuning the pure component parameters for lipids data. Figure 38-40 shows the results obtained for hexanoic acid and Figure 41-43 shows the results obtained for ethyl nonanoate.

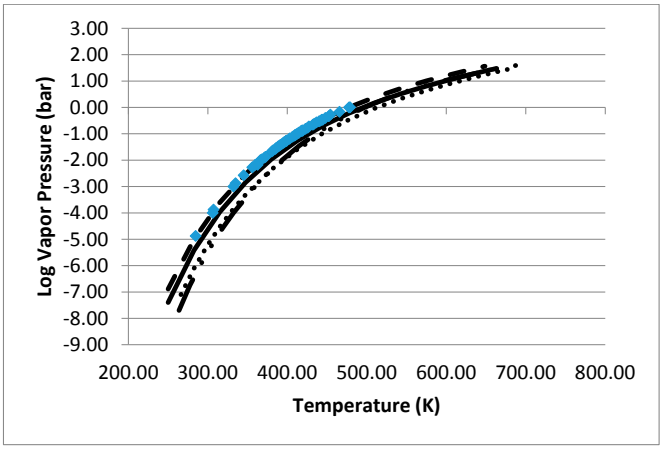

Figure 38: Comparison between the pure component parameters for PC-SAFT model in the calculation of vapour pressure for hexanoic acid. ◆Experimental data (CAPEC_Lipids_Database); _._ Reference from literature: Soo [109]; ….. Previous values; __ New parameters considering the groups; _ _ _ New parameters before consider the groups.

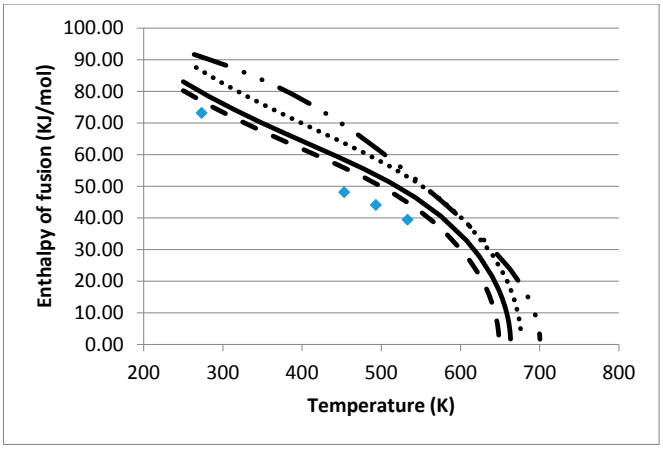

Figure 39: Comparison between the pure component parameters for PC-SAFT model in the calculation of enthalpy of fusion for hexanoic acid. ◆Experimental data (CAPEC_Lipids_Database); _._ Reference from literature: Soo [109]; ….. Previous values; __ New parameters considering the groups; _ _ _ New parameters before consider the groups.

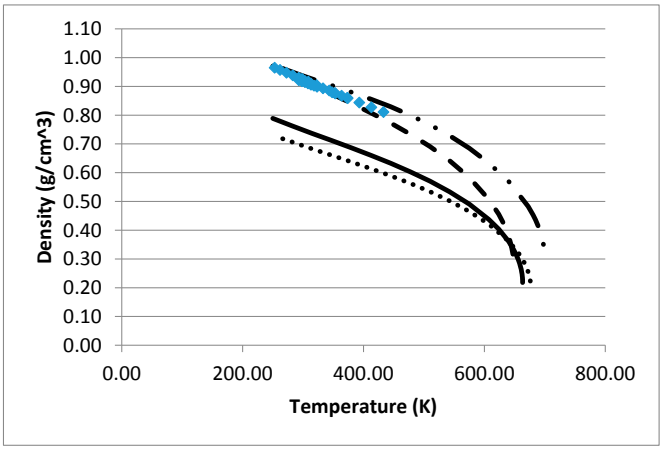

Figure 40: Comparison between the pure component parameters for PC-SAFT model in the calculation of density of fusion for hexanoic acid. ◆Experimental data (CAPEC_Lipids_Database); _._ Reference from literature [109]; ….. Previous values; __ New parameters considering the groups; _ _ _ New parameters before consider the groups.

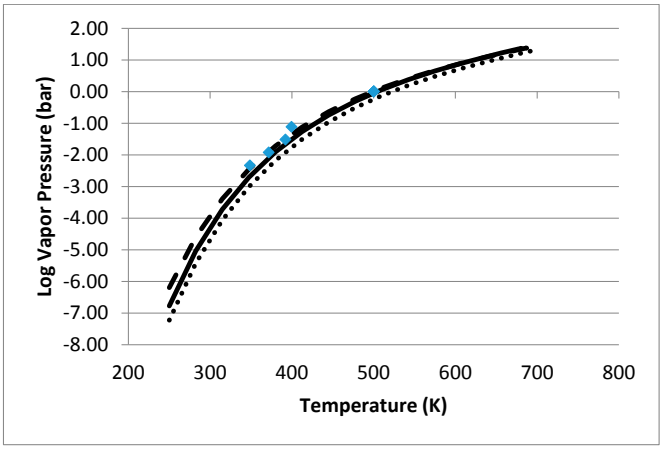

Figure 41: Comparison between the pure component parameters for PC-SAFT model in the calculation of vapour pressure for ethyl nonanoate. ◆Experimental data (CAPEC_Lipids_Database); ….. Previous values; __ New parameters considering the groups; _ _ _ New parameters before consider the groups.

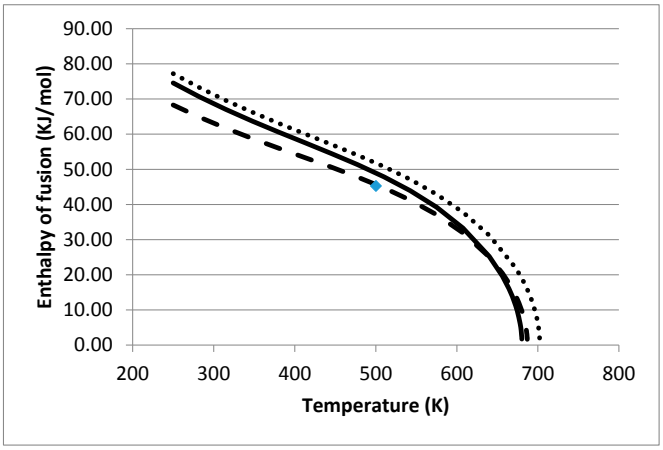

Figure 42: Comparison between the pure component parameters for PC-SAFT model in the calculation of enthalpy of fusion for ethyl nonanoate. ◆Experimental data (CAPEC_Lipids_Database); ….. Previous values; __ New parameters considering the groups; _ _ _ New parameters before consider the groups.

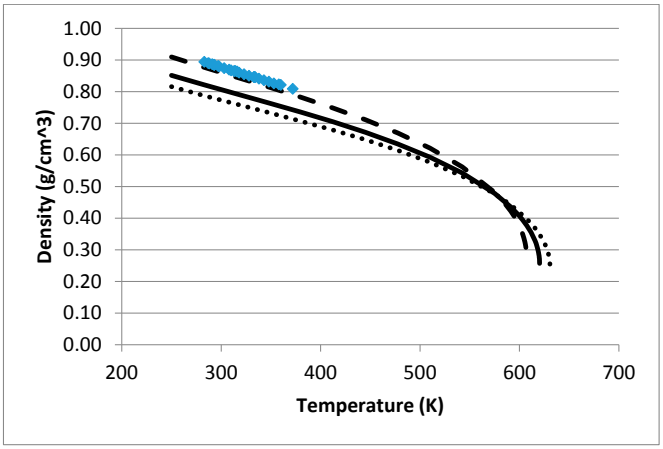

Figure 43: Comparison between the pure component parameters for PC-SAFT model in the calculation of density for ethyl nonanoate. ◆Experimental data (CAPEC_Lipids_Database); ….. Previous values; __ New parameters considering the groups; _ _ _ New parameters before consider the groups.

Improvement in the PC-SAFT model calculations for all the considered properties (vapour pressure, enthalpy of fusion and density) with respect to the previous values of pure component parameters inserted in ICAS was observed. This is due the fact of the preivous parameters may not be fine-tuned with lipids data. Also it is possible to observe higher deviations for density calculation after applying the group contribution approach for all cases, before and after fine-tune of the pure component parameters (m_i(-), σ_i (Å) and ε_i / k (K)).

Few authors have reported pure component parameters values in literature. Soo [109] have utilized the association parameter in calculations involving hexanoic acid. In Figures 38 and 39, it is possible to observe that good results in model presentation of properties such as vapour pressure, enthalpy of fusion and density without consider the association parameters could be obtained.

Chapter 5. Thermodynamic consistency tests

In some cases it is possible to visualize the uncertainty present in certain data set, but for many of the available data sets in literature it is not possible to guarantee the quality of the experimental data only by the graphic visualization. Considering this, thermodynamic consistency tests were used to analyze the available phase equilibria data.

5.1 Thermodynamic consistency tests for VLE data

TDE program developed at NIST by Frenkel et al. [132–138] were considered for testing consistency of VLE data. This software includes all VLE data points or data sets; if data are found to be inconsistent a lower quality factor ($Q_{test,i}$) is assigned to them. The Van Ness area test (Q_{test1}), the area or Herington test (Q_{test2}), the point or differential Test (Q_{test3}), an infinite dilution test (Q_{test4}), and a pure component property test (Q_{test5}) are included. In Q_{test5} the consistencies of the end-points (x = 0 and 1) of the VLE data are considered by comparing measured or extrapolated total pressures with pure component vapour pressures. The advantage of this test is that it applies to both TPx and TPy data. For the consistency tests requiring activity coefficients, the quality of regression to appropriate GE-based models indicates quality of an experimental data set. And an example of the results obtained for a mixture containing lipids (myristic acid and palmitic acid and three different references found in literature) can be seen in Figure 44.

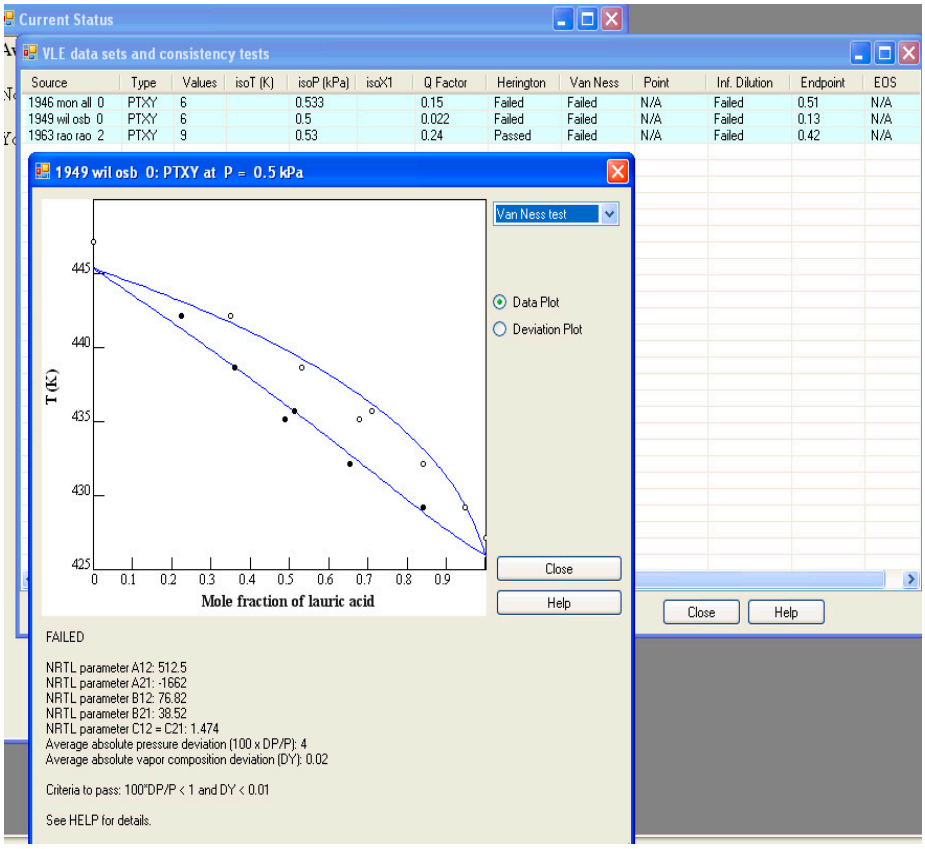

Figure 44: Example of experimental data analysis for a lipid system using ThermoData Engine (TDE) program.

Applying the TDE software (Frenkel et al. . [132–138]) to lipid data, a large percentage have failed in the consistency tests. Among the 92 VLE data sets at different pressure, temperature and range of molar fraction analyzed for lipid systems, the average of the quality factor was 0.228 with 1.0 being maximum and 0 being minimum. Only 9 systems exceeded the criteria associated with the above consistency tests. In fact, 23 of the systems had quality factors less than 0.05 while only 3% of the data sets had quality factors higher than 0.5. Regardless, our regressions found better defined parameters and a smaller uncertainty in the parameter values than in previous studies.

5.2 Thermodynamic consistency tests for SLE data

“SLE data sets” are characterized as those covering the entire composition range from the limits of pure component melting points. The label “Solubility systems” was used

for those data-sets of limited composition range, where only one solid component precipitates (see below). SLE systems can have similar types of errors to those for VLE data-sets. However, consistency tests based on the Gibbs-Duhem Equation cannot be applied for solubility systems because there are no states where both component activities can be obtained simultaneously. In addition, there is normally a strong temperature dependence of the data, the pure component melting point limits are less well-identified than pure component vapour pressures, and the models typically used for describing non-ideality in VLE may not be reliable for solid solubilities. Given this situation, two tests for quality were developed for SLE data sets and applied to the binary systems of the CAPEC_Lipids_Mixtures_Database and DECHEMA® database. Test 1 ($Q_{SLE\cdot Test1}$) for SLE data is similar to the Q_{test5} of the TDE program for VLE data. It evaluates whether the mixture data asymptote to the pure component melting points. The quality factor for $Q_{SLE\cdot Test1}$ is calculated as:

$$Q_{SLE\cdot Test1} = \left(\frac{2}{1000\left(\Delta t_1^0 + \Delta t_2^0\right)} - U \right) \tag{24}$$

where

$$\Delta t_1^0 = \left| \frac{T_{m1}^0 - t_1^0}{t_1^0} \right| \tag{25}$$

$$\Delta t_2^0 = \left| \frac{T_{m2}^0 - t_2^0}{t_2^0} \right| \tag{26}$$

and

$$U = \frac{1}{10}(\theta_1 + \theta_2) \tag{27}$$

In Eqs. (24-27), T_{mi}^0 is the measured or extrapolated melting point of the mixture in the limit $x_i \to 1$, x_i is the mole fraction of the compound *i*, t_i^0 is the pure melting point temperature of compound *i* and θ_i is the absolute uncertainty in t_i^0.

A total of 358 data sets from the DECHEMA® database for solid solubility data and 70 SLE data sets in CAPEC_Lipids_Mixtures_Database were analyzed with the above test. Test 2 ($Q_{SLE\cdot Test2}$) is similar to that of Van Ness [124] for VLE systems where the ability of a model to describe the data is assessed. The usefulness of this test depends on the reliability of the model for the description. Here a new approach has been used for SLE and solubility data of binary systems.

In order to evaluate whether any data might be given a lower Q_{SLE} due to the model insufficiency instead of data error, an alternative activity coefficient model (Test 3 or $Q_{SLE\cdot Test3}$) was developed. The parameters for this model are the 2-parameter temperature dependent for calculation of activity coefficients at infinite dilution and a 1-parameter theoretically-based term for solute non-ideality relative to infinite dilution. Though this is not a rigorous thermodynamic consistency test, it can display variations in continuity of data for solubility with temperature and composition, as well as indicate errors in the pure component limits. It is also a potential approach to predict of solute activities, though this has not been attempted here.

The development of the proposed test starts with the usual relation for the binary mixture solubility of a pure solid in a liquid solution [199]:

$$\ln x_1\gamma_1 = \frac{\Delta H_{fus}}{R}\left(\frac{1}{T_m}-\frac{1}{T}\right) \tag{28}$$

where ΔH_{fus} is the enthalpy of fusion, T_m is the melting temperature, x_1 is the molar fraction of component 1, γ_1 is the activity coefficient of component 1 for the pure component (Lewis-Randall) standard state, and T is the system temperature. Rigorous additional terms on the right hand side of equation (28) involving the difference in heat capacities of the solid and sub-cooled liquid have been ignored since they generally are small [199]. Further, it is assumed that no pure solid structure transitions occur between T and T_m. Knowledge of the thermodynamic data and property models that consider the structure of the solid phase and consequently the polymorphism that may be present, has been studied by others (see for example, [21,200–208]). For example, triacylglycerols (TAGS), representing around 95% of the vegetable oils of interest, have been reported to have three polymorphs [200]. A thermodynamic model for fats and oils that consider the polymorphism of TAGS has been reported by Won [203]. Implementation of this element of the data treatment will be included in future work, perhaps leading to slight revised parameters, but omitting it should not materially affect the outcome of the current procedures.

For dilute solutions, the Henry's Law standard state can be more reliable than the pure-component standard state, since the unsymmetric convention activity coefficients, designated by γ_i^* are often very close to unity. γ_i^*; it is related to γ_i by:

$$\ln\gamma_i^* = \ln\gamma_i - \ln\gamma_i^\infty \tag{29}$$

where the infinite dilution activity coefficient is $\ln \gamma_i^{\infty} \equiv \lim_{x_i \to 0} \gamma_i$. This property is a function only of temperature or density and is often modelled with 2 parameters, a and b, simply as

$$\ln \gamma_1^{\infty} = a + b/T \tag{30}$$

Fluctuation solution theory (FST) [209] shows that an expansion of the unsymmetric convention activity coefficient about infinite dilution has composition terms of the following form:

$$\ln \gamma_1^{*} = -f_2^0 \left(2x_1 - x_1^2\right) - f_3^0 \left(\frac{3}{2} x_1^2 - x_1^3\right) + \ldots \tag{31}$$

where the coefficients f_2^0 and f_3^0 are related to integrals of infinite-dilution molecular correlation functions, and are functions only of temperature or density. Their theoretical evaluation is not possible for lipids, so they will be treated as constants or weak functions of temperature.

Combining equations (29) – (31) yields an expression for solubility:

$$\ln x_1 = \frac{\Delta H_{fus}}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) + f_2^0 \left(2x_1 - x_1^2\right) + f_3^0 \left(\frac{3}{2} x_1^2 - x_1^3\right) + a + b/T \tag{32}$$

Sets of SLE data have been regressed with constant parameters, a and b, along with either constant f_2^0 or with $f_2^0 = c/T$. In all cases, the term in f_3^0 had no influence on quality of the data fitting, and so could be neglected. The temperature dependent $f_2^0 = c/T$ was more accurate. Thus the FST model is

$$\ln x_1 = \frac{\Delta H_{fus}}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) + \frac{c}{T}\left(2x_1 - x_1^2\right) + a + b/T \tag{33}$$

Our regression strategy was to choose a value of c and regress for a and b, modifying c until a minimum objective function value was found.

Once parameter values are set, equation (33) can also be iteratively solved for the temperature:

$$T = \frac{1}{\ln x_1}\left[\frac{\Delta H_{fus}}{R}\left(\frac{T}{T_m} - 1\right) + c\left(2x_1 - x_1^2\right) + aT + b\right] \tag{34}$$

There are 358 solubility data sets in the DECHEMA® database and 70 SLE data sets of lipids in the CAPEC_Lipids_Mixtures_Database that were evaluated with Test 3 ($Q_{SLE\cdot Test3}$) by regressing for the 3 parameters, a, b, and c.

Comparing regressions from the NRTL and the FST models showed some differences. For example systems with noisy data were routinely better represented. A relation for Q_{SLE} associated to Test 2 and Test 3 was developed. The quality factor is:

$$Q_{SLE\cdot Test\,2/3} = \left(\frac{1}{1 + \mathrm{AAD}(\%)} \right) \tag{35}$$

where AAD(%) is the deviation for the selected objective function of the regression (see below).

The use of the four tests provides the overall quality factor for SLE data:

$$Q_{SLE} = 0.33 Q_{SLE\cdot Test1} + 0.33 Q_{SLE\cdot Test2} + 0.33 Q_{SLE\cdot Test3} \quad , \; Q_{SLE} \le 1 \tag{36}$$

Table 24 gives examples of the results for cases where the term in U is included and where it is not. It is important to note that here that the SLE data do not account for errors that might be due to assigning the wrong pure solid structure. The range of $Q_{SLE\cdot Test1}$ from very low to very high values for the myristic acid systems using data reported by Boros [180].

Test 2 is similar to that of Van Ness [124] for VLE systems where the ability of a model to describe the data is assessed. The usefulness of this test depends on the reliability of the model for the description. Our earlier work used common GE forms such as NRTL. Here a new approach has been used for SLE and solubility data of binary systems, as described below. At the simplest level, the models have three fitted parameters.

Table 24: Examples of results for the pure component SLE thermodynamic consistency test (Test 1), 2 data sets per binary mixture.

Compounds		T_{m1}^{0}	T_{m2}^{0}	Δt_1^0	Δt_2^0	$Q_{SLE\text{-}Test1}$ without U	$Q_{SLE\text{-}Test1*}$	Ref.
Lauric Acid (1) t_1^0 =316.97 ±0.04	Myristic acid (2) t_2^0 =327.31±0.04	289.6	304.42	0.0863	0.0699	0.01	0.01	[180]
		316.94	327.48	0.0001	0.0005	1.00	0.99	[177]
Myristic acid (1) t_1^0 =327.31±0.04	Stearic acid (2) t_2^0 =342.47 ±0.01	327.48	341.91	0.0005	0.0016	0.95	0.93	[180]
		328.88	343.98	0.0048	0.0044	0.22	0.20	[181]
Myristic acid (1) t_1^0 =327.31±0.04	Palmitic acid (2) t_2^0 =335.64±0.04	328.88	335.44	0.0048	0.0006	0.37	0.36	[181]
		327.07	335.02	0.0007	0.0018	0.80	0.79	[180]
Methyl palmitate (1) t_1^0 =302.71±0.46	Methyl stearate (2) t_2^0 =311.84±0.63	302.83	311.83	0.0003	0.0001	1.00	0.97	[210]
		303.93	314.07	0.0040	0.0072	0.18	0.15	[179]

* The final value of the quality factor ($Q_{SLE\text{-}Test1}$) considering the uncertainty of the pure component (U) in Equations (1) and (4). Note that the quality factor varies between 0.1 and 1.

The results from fitting the NRTL model parameters to SLE data are given in Table 25 for all systems analyzed (DECHEMA® and CAPEC_Lipids_Mixtures_Database). The columns are for different ranges of ARD (%). Essentially all systems had ARD (%) lower than 10%.

Table 25: The absolute deviation for NRTL model found for the systems analyzed in temperature calculation.

	ARD (%) =<0.05	0.05< ARD (%) =< 0.1	0.1< ARD (%) =< 0.5	0.5< ARD (%) =< 1	1< ARD (%) =< 2	2< ARD (%) =< 3	3< ARD (%) =< 5	5< ARD (%) =< 10	10< ARD (%) =< 20	ARD (%) =>20	Total number of systems
Number of Systems	7	13	115	76	90	26	20	10	1	0	358
%	1.96	3.63	32.12	21.23	25.14	7.26	5.59	2.79	0.28	0.00	100

There are 358 solubility data sets in the DECHEMA® database and 70 SLE data sets of lipids in the CAPEC_Lipids_Mixtures_Database that were evaluated with Test 2 and 3 by regressing for the 3 parameters, a, b, and c of Equations (32 and 33). Results for both the NRTL and FST models for some representative systems are shown in Figure

45 with the NRTL model being the solid lines and the FST model being the dotted lines. As found previously, many of the systems had large ARD (%) values, including those of systems C) and F) in Figure 45, due to noise in the data. It can be seen that the FST model is always more accurate, even when the data are noisy, suggesting that the temperature and/or composition dependence of the NRTL model is not highly accurate for these cases.

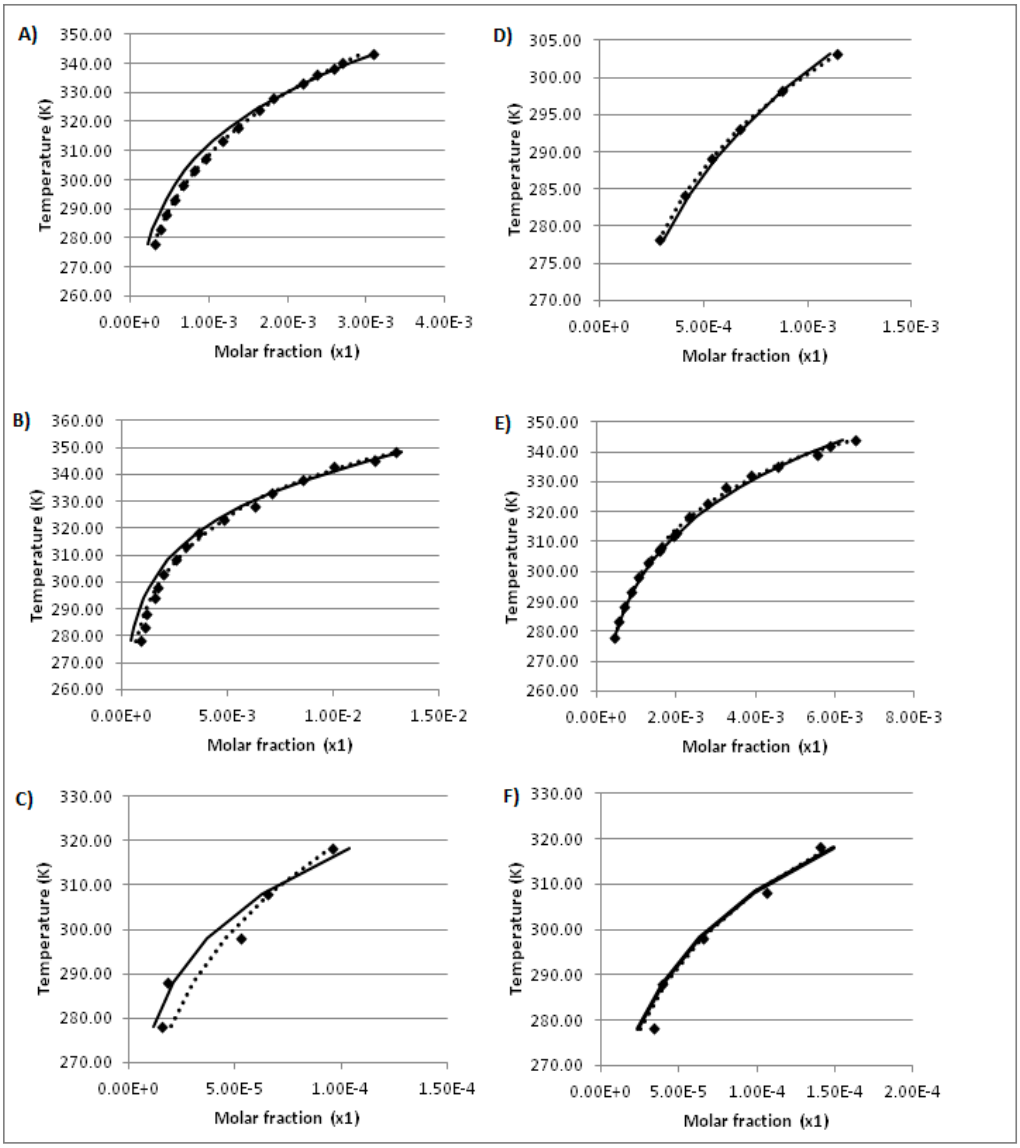

Figure 45: A) Solubility of L-Aspartic acid(1) in water(2)[56]; B) Solubility of DL-Glutamic acid(1) in water(2) [211]; C) Solubility of 4,5-Dichloroguaicol(1) in water(2) [212]; D) Solubility of 4-Hydroxibenzoic acid(1) in water(2) [211]; E) Solubility of DL-Aspartic acid(1) in water(2) [211]; F) Solubility of 4.6-Dichloroguaiacol(1) in water(2) [212]. ◆Experimental data; — NRTL model; - - - FST model.

These success for solid solubility descriptions suggested applying the model to lipid SLE systems covering the entire composition range. Figures 46 and 47 show that the dashed line for FST is at least as close to the data symbols as is the solid line for NRTL, as was also found for eutectic and peritectic systems. This might seem unexpected, but it is due to the similarity of the compounds involved, differing only in chain length and not functional group. Therefore, the deviations from ideal solution are relatively small and are well-described by the simple. This probably would not be the case for substances with significantly different functional groups, but these are often not fully miscible in the solid phase and therefore have heterogeneous solubility behaviour.

Eutectic points are usually observed in SLE of lipid systems, as can be seen in Figure 46. However, peritectic points can be observed as in Figure 47 for the myristic acid - stearic acid system. A characterization of peritectic point can be found in [213]. Costa et al. [177] report other mixtures where peritectic points occur, such as, binary systems of capric acid-myristic acid and lauric acid-myristic acid mixtures, mainly when the difference between the number of carbon atoms of the fatty acid chains in the mixture is less than six. Costa et al. [177] demonstrated that the Slaughter and Doherty [213] approach for the prediction of the solid phases with an equilibrium constant for acid interactions provided good fits of the phase diagrams of systems with peritectic points. While the Slaughter and Doherty method [213] does not follow the Gibbs-Duhem equation, it has been used by many authors with good results, as in the work of Rocha and Guirardello [214].

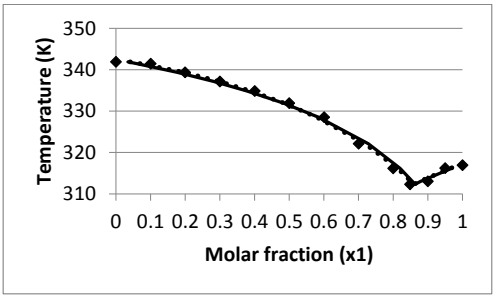

Figure 46: Lauric acid(1) and stearic acid(2) SLE [177] ◆Experimental data; — NRTL model; - - - FST model.

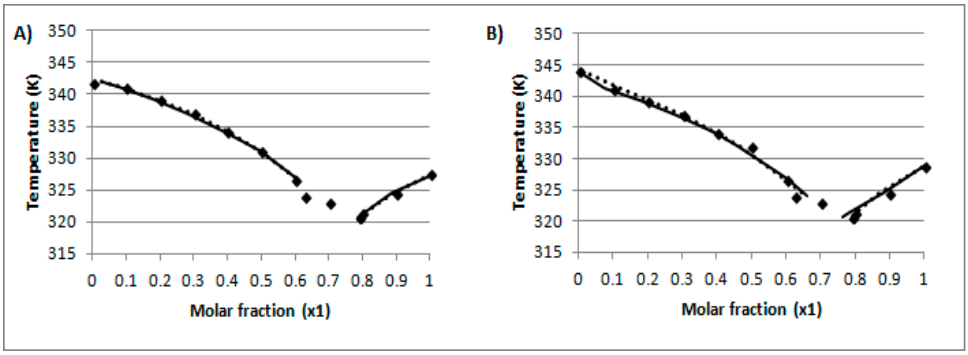

Figure 47: Myristic acid(1) and stearic acid(2) SLE ◆Experimental data A)[180] B)[181]; — NRTL model; - - - FST model.

Table 26 collects the results found for the systems of Figures 45 – 47. There is a wide range of values with only one system, 4-Hydroxybenzoic acid(1) and water(2), that yields a $Q_{SLE\cdot Test2} > 0.5$.

The quality factors obtained from the thermodynamic consistency tests are given in Appendix 4 for VLE and SLE data and lipids systems.

Table 26: Quality factors for SLE systems from Test 2 and 3.

Solute (1) in Solvent (2)	$Q_{SLE\cdot Test2/3}$	Reference
L-Aspartic acid(1) in water(2)	0.40	[211]
DL-Glutamic acid(1) in water(2)	0.14	[211]
4,5 Dichloroguaicol(1) in water(2)	0.04	[212]
4-Hydroxybenzoic acid(1) in water(2)	0.81	[211]
DL-Aspartic acid(1) in water)	0.34	[211]
4,6-Dichloroguaicol(1) in water(2)	0.11	[212]
Lauric acid(1) and Myristic acid(2)	0.51	[177]
Lauric acid(1) and Stearic acid(2)	0.19	[177]
Myristic acid(1) and Stearic acid(2)	0.23	[180]
Myristic acid(1) and Stearic acid(2)	0.20	[181]

5.3 Software implementation (TDEEquilibria) of the proposed SLE thermodynamic consistency tests

The proposed methodology for SLE thermodynamic consistency tests was combined with the methodology that considered a algorithm for experimental data analysis and were proposed by Kang et al. [131]. Databases such as NIST-TDE®, DIPPR® and DECHEMA® were also combined to validate the proposed tests. The SLE consistency test and data evaluation is performed in a software containing option for data analysis, model analysis and parameter regression. The same database for SLE combined with the quality factor obtained from the thermodynamic consistency tests were utilized for original UNIFAC model parameter regression, now considering a high weight for SLE systems in comparison with VLE and LLE systems, aiming improve the representation of experimental data for this kind of phase equilibrium (SLE).

The user has also the possibility to consider only the tests that are applicable. In the case of solid solubility data for example, these test are only $Q_{SLE\cdot Test2}$ (Van Ness) and $Q_{SLE\cdot Test3}$ (FST). The end-points are not given in many solid solubility data available in literature. Comparing regressions from the NRTL and the FST models point to some differences. For example, systems with noisy data are routinely better represented by the FST model. The interface of TDEEquilibria program developed by the group of Prof. Kang in Korea University together with NIST is shown in Figure 48.

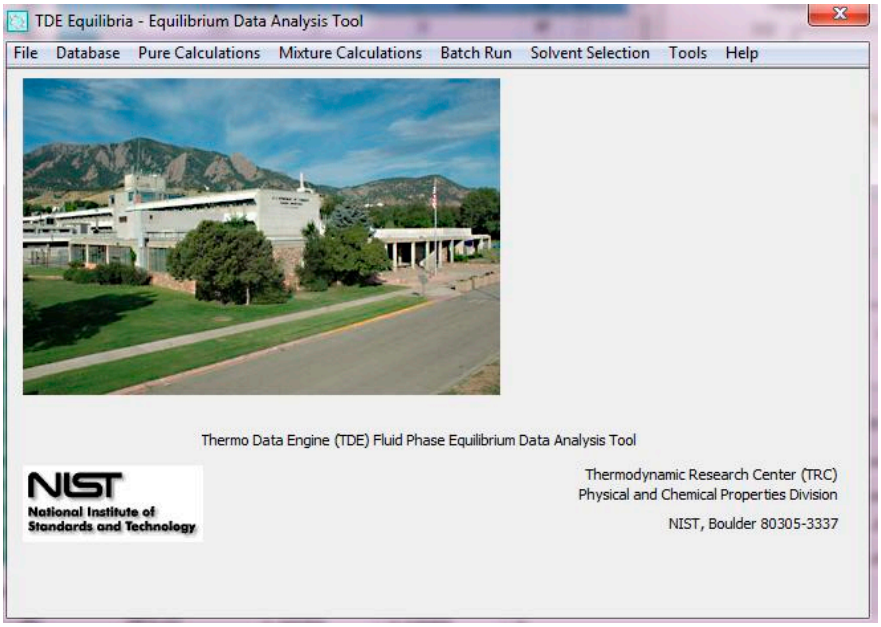

Figure 48: TDEEquilibria program.

A lipid data set containing peritectic point is selected for analysis with the methodology for the SLE thermodynamic consistency tests and the results are highlighted in Figure 49. The model performance observed here is confirmed by the results found in the uncertainty analysis of the parameter regression performed for NRTL, UNIQUAC, UNIFAC and FST models, where the regressed parameters play an important role in the intermediate points for NRTL, UNIQUAC and original UNIFAC models, but for FST model, the parameters also influence the end-points (x1=0 and x1=1). It is possible to visualize in Figure 49 that NRTL model tries to follow the tendency of the pure component data-points, which affects the model representation of experimental data.

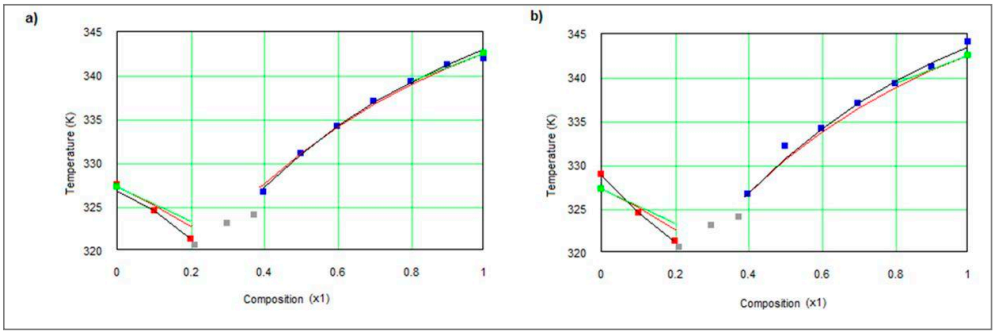

Figure 49: Binary mixture of myristic acid (1) + stearic acid (2) ■ a) Boros [180] and b) Costa [181] at pressure equal 101.325KPa ■Data points do not used in the calculation (between eutectic and peritectic data points) ■Test 1 (Pure Test), —Test2 (Slope), —Test3 (NRTL model capability) and —Test 4 (FST).

One example was selected to exemplify the SLE data analysis utilizing the TDEEquiliria software and is given in Figure 50. It is important to highlight that one more SLE thermodynamic consistency test were included in the software and is part of the work developed by Kang et al. [215]. In Kang et al. work [215], the authors bring an algorithm for experimental data analysis including VLE, SLE and LLE systems.

Application of the software for the extensive collection of SLE data sets demonstrated gives a general idea of the quality of the available data. This software can be a good option of a global data validation process (thermophysical and thermochemical property data).

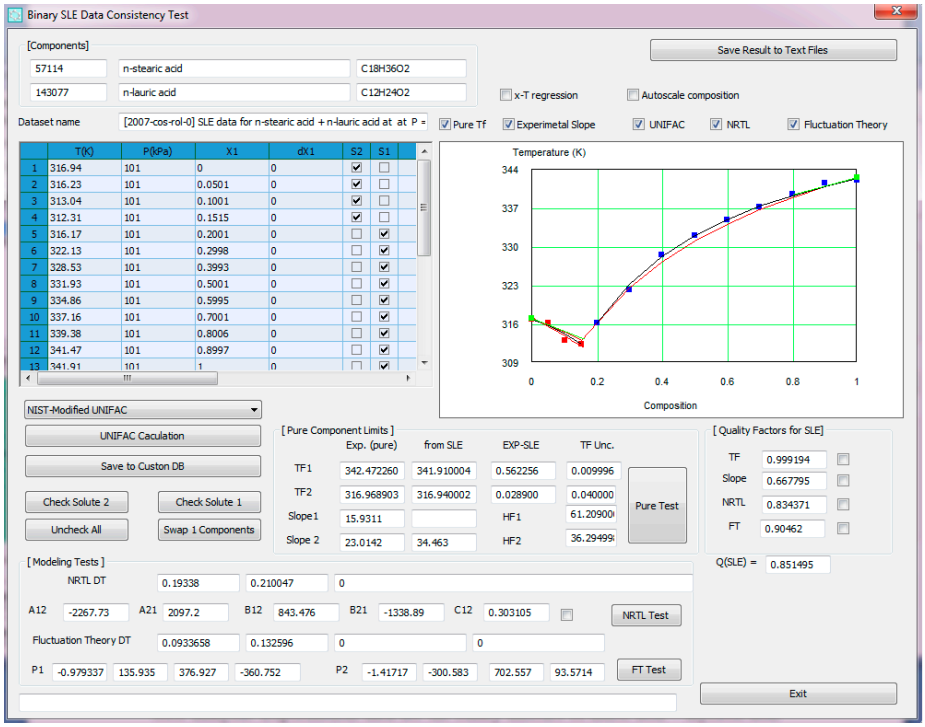

Figure 50: Screen shot from the software developed for thermodynamic consistency tests analysis. Experimental data for the binary mixture of stearic acid (1) + lauric acid (2) ■Experimental data: Costa et al. [177] at pressure equal 101.325KPa using ■Test-1 (Pure Test), —Test-2 (NRTL model capability) and —Test-4 (FST).

Chapter 6. Iodine value and cloud point estimation for lipids

The first step to develop the methodology for iodine value and cloud point estimation for lipids was the data collection. Experimental iodine values for vegetable oils containing the fatty acids information as composition have been reported by many authors [143,145–148,216–220]. In total 185 different sources of experimental iodine values were compared with theoretical iodine values calculated considering the incidence of fatty acids in each vegetable oil. The theoretical iodine values of the fatty acids were calculated for the fatty acids considering the quantity of iodine necessary for the 100g of the compound in a stoichiometric and in a equilibrium based reaction. For biodiesel, experimental iodine values can also be found in literature [144,161,217,221,222], in this case with the methyl esters information as composition. In total 22 different sources of experimental iodine values were compared with the theoretical iodine value calculated considering the incidence of methyl esters in each biodiesel. For vegetable oils, cloud point values could be found in 22 different sources [143,144,223–225], also containing the information of the fatty acids composition. However, for biodiesel 32 different sources [156,161,217,222,223,226–232] contain the information of the methyl esters composition. A trend between iodine value and cloud point was observed, what justify the use of a correlation between iodine value and cloud point values, using a simple linear relationship:

$$Cp_{calc} = a.IV + b \tag{37}$$

Where Cp_{calc} is the calculated cloud point, IV is the iodine value and a and b are regressed parameters.

In Table 27, the theoretical iodine value is given for the fatty acids presented in the vegetable oils considered in this part of the work (due the fact of availability of experimental data, as cited before in Chapter 3) and were calculated considering the quantity of iodine necessary for the 100g of the compound in a stoichiometric and equilibrium based reaction. The total ARD(%) obtained between the experimental and calculated values is 3.334%. Figure 51 shows the experimental versus the calculated for

iodine values and vegetable oils. It is possible to observe good representation of the experimental data for the correlation with pure component property.

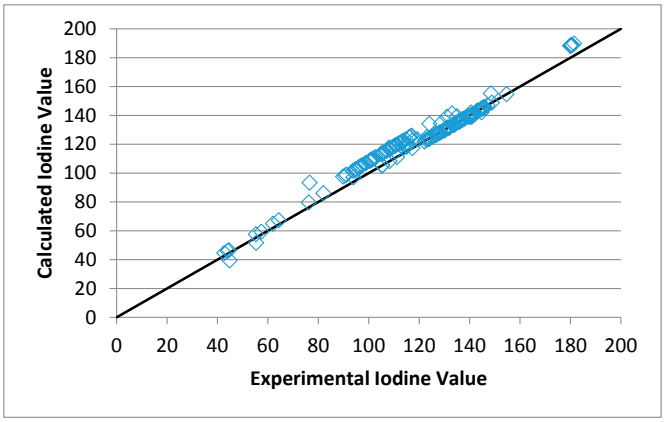

Figure 51: Scatter plot of iodine values for vegetable oils.

The calculation of iodine value using the pure component property and their composition in the mixture was also performed for biodiesel. The theoretical iodine value calculated for methyl ester can be seen in Table 27. The total average ARD(%) obtained between the experimental and calculated values is 2.106%. The experimental versus the calculated for iodine values are showed in Figure 52 for biodiesel mixtures. It is also possible to observe good representation of the experimental data for the correlation with pure component property. Lower quantity of experimental data for iodine value is available in literature for vegetable oils in comparison with biodiesel.

Table 27: Iodine values for fatty acids and methyl esters.

Carbon number	Iodine value	
	Fatty acids	Methyl esters
C16:1	99.76	94.55
C18:1	89.85	85.60
C18:2	181.00	172.38
C18:3	273.56	260.36
C20:1	81.74	78.81
C22:1	69.65	71.98
C24:1	69.23	66.68

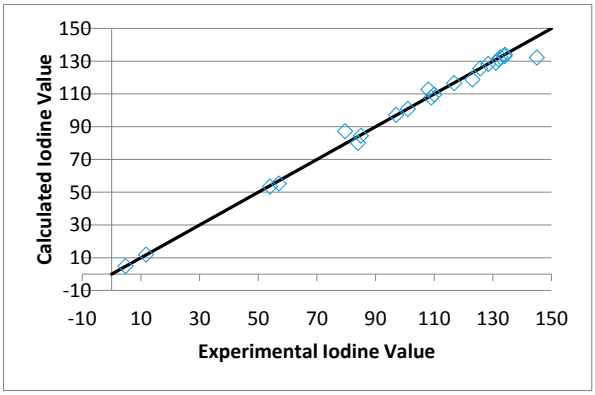

Figure 52: Scatter plot of iodine values for biodiesel compounds

A trend between iodine value and cloud point was observed for each vegetable oils and biodiesel compounds, as can be seen in Figure 53 and 54, respectively.

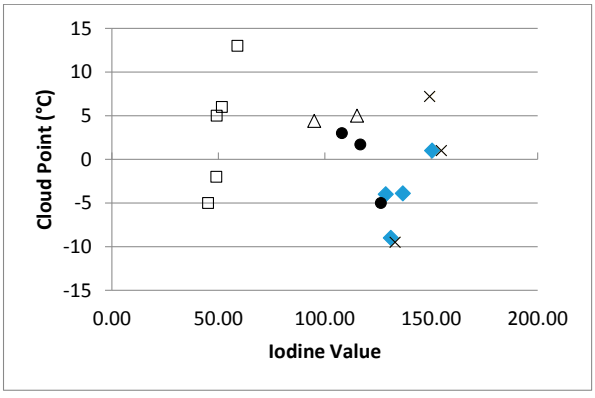

Figure 53: Iodine value versus cloud point for different vegetable oils: ◆Soybean, ●Cottonseed, ΔPeanut, ×Sunflower and □Palm.

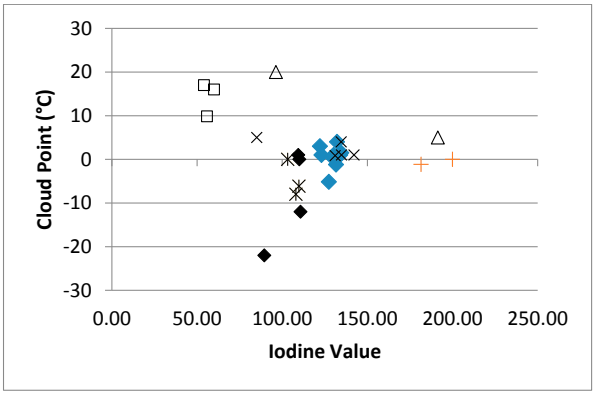

Figure 54: Iodine value versus cloud point for different biodiesels: ◆Soybean, ΔPeanut, × Sunflower, *Rapseed, □Palm, ◆Canola, and +Linseed.

The regressed parameters obtained in the linear correlation can be seen in Table 28. The results found for cloud point calculation present ARD(%) of 1.810 for vegetable oils and 1.785 for biodiesel. The experimental cloud point values versus the calculated ones are shown in Figure 55 and 56 for vegetable oils and biodiesel compounds, respectively. The results obtained for cloud point calculation showed higher deviation in comparison with experimental value than the calculated iodine values, what can be explained by the use of different methods of measurements of the cloud point property (visual or automatic, for example). As reported by Hammami et al. [233] for cloud point values reported for oil, new techniques are necessary to assure reliable experimental measurements, once the precipitation kinetics and solid phase detection limits should also be considered. Coutinho and Daridon [234] also have showed the limitations of cloud point measurements for oils.

Table 28: Coefficients for cloud point calculation using Eq. 35.

Mixtures		a	b
Vegetable Oil	Soybean	0.3396	-50.3769
	Cottonseed	-0.4420	51.6085
	Peanut	0.0298	1.5656
	Sunflower	0.6072	-88.8681
	Palm	1.2889	-62.0334
Biodiesel	Soyben	0.0381	-4.2568
	Peanut	-0.1577	35.1845
	Sunflower	-0.0641	10.4137
	Linseed	0.0622	-12.4361
	Rapseed	-1.0847	111.3289
	Palm	0.1249	7.2180
	Canola	0.8607	-98.5160

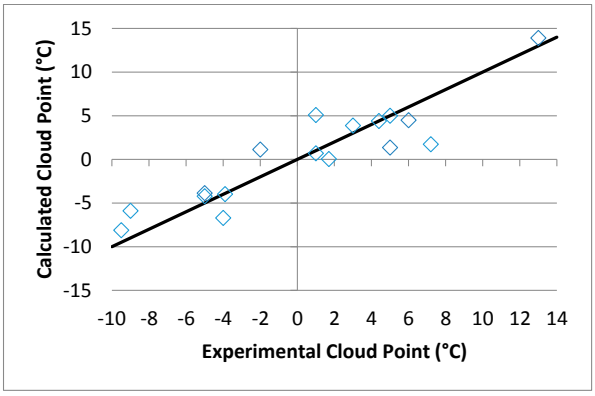

Figure 55: Scatter plot of cloud point values for different vegetable oils

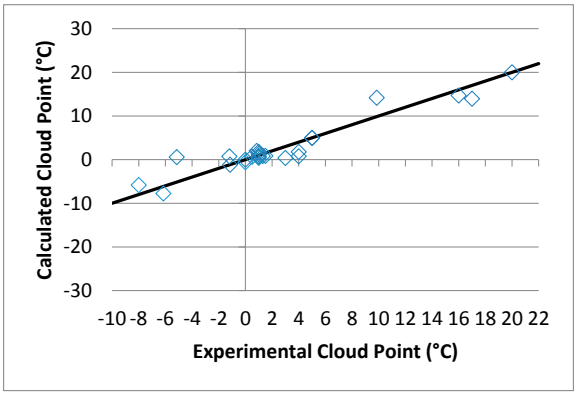

Figure 56: Scatter plot of cloud point values for different biodiesel compounds

Chapter 7. Experimental work procedure

In this PhD project, the DSC technique was used for measuring boiling points of two binary fatty mixtures composed of a monoacylglycerol (monocaprylin) and a fatty acid (palmitic acid – system 1) or a fatty methyl ester (methyl stearate – system 2) at two sub-atmospheric pressures (1.2 KPa and 2.5 KPa). Two thermodynamic consistency tests were applied to verify the quality of the measured data. The pure component consistency test ($Q_{test,5}$ of the TDE program developed by NIST [132–138]) was used to test the consistencies of the pure component end-points of the VLE data, and a variation of Van Ness Test [124] (Qtest,1 of program TDE developed at NIST), that checks the consistency of the measured data as represented by a flexible thermodynamic trial function. The measured data was correlated by the Wilson, NRTL, and UNIQUAC models. The original UNIFAC was first checked for their predictive capability and then fine-tuned in terms of new regressed binary interaction parameters for the main groups found in the chemical systems studied.

7.1 Materials

The reagents monocaprylin (CAS Registry no. 19670-49-6), palmitic acid (CAS Registry no. 57-10-3) and methyl stearate (CAS Registry no. 112-61-8) with 99% purity were purchased from Nu-Check Prep. The reagent n-tetradecane (CAS Registry no. 629-59-4) with 99 % purity was purchased from Sigma-Aldrich. The samples were placed in aluminum crucibles (pans + lids) purchased from TA Instruments. Following the procedure described by Matricarde Falleiro et al. [170,171] and Damaceno et al. [168], a pinhole of diameter of 800 μm was made on each lid using a system consisting of a fixation assembly, mandrel and drills. A small tungsten carbide ball with a diameter of 1000 μm was obtained from the disassembly of a ballpoint pen, and placed over the pinhole [168]. In Figure 57, it is possible to better visualize the Ballpoint pen and the pinhole and in Figure 58, it is possible to visualize the top of the DSC equipment where the reference and the sample are placed.

Figure 57: Ballpoint pen being placed over the pinhole.

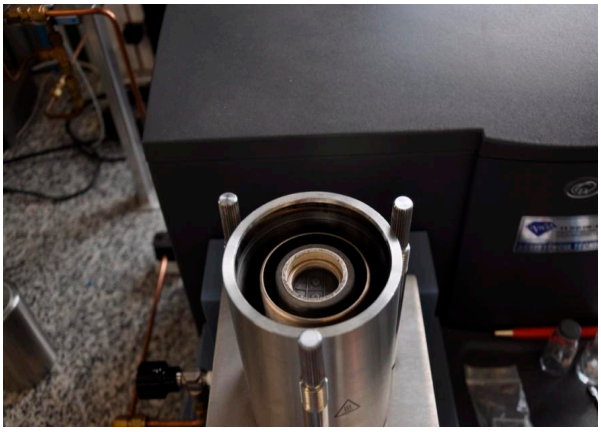

Figure 58: View from the top of the DSC equipment.

7.2 Sample preparation

Each of the two fatty systems considered in this work were prepared by mixing known amounts (in grams) of the pure components in an analytical balance (Model AS220 – Radwag) to obtain approximately 0.2 g of the binary mixture. The data point sample of approximately 0.2g is can be seen in Figure 59. In total, nine binary mixtures with molar fractions (x1) ranging from 0.1 to 0.9 of the more volatile compound are produced in intervals of 0.1 mole fractions to cover the entire range of compositions in an isobaric Tx diagram. The pure component data, that is, molar fractions of the more

volatile compound equal to 0 (x1 = 0) and equal to 1 (x1 = 1) were also considered. In the case of system 1, an additional binary mixture with a molar fraction of the more volatile compound equal to 0.0554 is produced, giving thereby, ten binary mixtures. Microsamples (4 – 5 mg) were obtained from each binary mixture with micropipets of 5.10-10 – 10.10-10 m3 (Model Research – Eppendorf), and then weighted in a microanalytical balance (Model C-33 - Thermo Scientific).

Figure 59: Binary mixtures containing approximately 0.2g each.

7.3 Apparatus

A schematic diagram of the experimental apparatus is given by Matricarde Falleiro et al. [170]. A Differential Scanning Calorimetry (DSC) Model Q20P – TA Instruments is connected to a vacuum system which consists of a trap to pressurize the vacuum line, a ballast tank to avoid pressure oscillations, a micrometer valve to adjust the pressure, a digital pressure gauge Model Rücken RMD, and a vacuum pump Model RV5 – Edwards [168]. A view from the top of the DSC equipment is shown in Figure 12. A computer was used to run the DSC and record data from each experiment. A computer is used to run the DSC and record data from each experiment. A press (Model SN6205 - TA Instruments) is used to seal the crucibles (pans + lids) [168].

7.4 Calibration

The baseline, cell constant and temperature were calibrated according to the standard methods and ASTM E1782-08 guidelines [235]. For the temperature calibration, indium and zinc standards purchased from TA instruments were used, following a run with a heating rate of 25 K min-1 at atmospheric pressure, and the melting point obtained were 431.62K (indium) and 692.37 K (zinc), respectively, which are in accordance with the International Practical Temperature Scale [236].

7.5 Experimental procedure

The employed experimental procedure follows the ASTM E1782-08 guidelines [237] with adjustments suggested by Matricarde Falleiro et al. [170,171] and followed by Damaceno et al [168]. A Differential Scanning Calorimetry (Model Q20P – TA Instruments) with a pressure cell (PDSC) and connected to a vacuum system was used to measure boiling points at selected pressures [168]. In each run, a pair of hermetically sealed crucibles with a pinhole on the lid, and a tungsten carbide ball over it is placed in the pressure cell. One empty of them is kept empty (as a reference) and the other is filled with a microsample (4-5 mg). The pressure cell was then subjected to a heating rate of 25 K min-1, raising the temperature from 300 to 700 K at constant absolute pressure. N-tetradecane was used to calibrate the pressure gauge. As the heating time was ended, the pressure cell was restored to ambient conditions. For each pressure selected in this work (1.2 KPa and 2.5 kPa), the boiling points of different molar fractions of each binary mixture were determined from the extrapolated onset temperature obtained from the thermal curves generated by the DSC software [168,170,171].

7.6 Results and discussion

Table 29 list the measured points for different molar fractions of the more volatile compound of system 1 (monocaprylin + palmitic acid) and of system 2 (monocaprylin + methyl stearate) at 1.2 kPa and 2.5 kPa together with expected standard uncertainties. Figures 60 and 61 show plots of measured isobaric vapour liquid equilibria for systems 1 and 2 at 1.2 KPa and 2.5 kPa, respectively.

Table 29: Experimental data for boiling points T/K with standard uncertainty u (T) for systems 1 and 2.

System 1 [monocaprylin (1)+ palmitic acid (2)]					System 2 [monocaprylin (1)+ methyl stearate (2)]				
Pressure[a]	1.2 kPa		2.5 kPa		Pressure[a]	1.2 kPa		2.5 kPa	
Molar fraction (x_1) [a]	T/K	u (T)/K	T/K	u (T)/K	Molar fraction (x_1) [a]	T/K	u (T)/K	T/K	u (T)/K
0.0000	483.15	0.54	498.35	0.16	0.0000	475.97	0.46	493.38	0.46
0.0554	478.11	0.31	494.10	0.37	0.1018	472.10	0.36	491.26	0.46
0.0991	475.96	0.36	491.78	0.31	0.1993	469.50	0.31	487.88	0.53
0.1938	472.16	0.42	488.90	0.51	0.3099	465.48	0.34	483.97	0.50
0.3035	468.14	0.75	486.66	0.16	0.4007	462.15	0.45	480.07	0.41
0.4065	466.36	0.43	485.43	0.51	0.5005	461.78	0.49	479.07	0.21
0.4991	464.66	0.43	483.40	0.06	0.6018	461.29	0.45	478.60	0.35
0.6033	464.24	0.32	482.02	0.43	0.7022	461.24	0.12	478.66	0.08
0.7016	463.47	0.40	480.97	0.44	0.7970	461.65	0.11	478.97	0.44
0.7852	463.08	0.55	480.35	0.37	0.8938	462.10	0.46	479.4	0.25
0.9031	462.67	0.40	480.07	0.34	1.0000	462.94	0.10	480.41	0.42
1.0000	462.94	0.10	480.41	0.42					

[a] Standard uncertainties are u (p) = 0.1 kPa and u (x) = 0.0004.

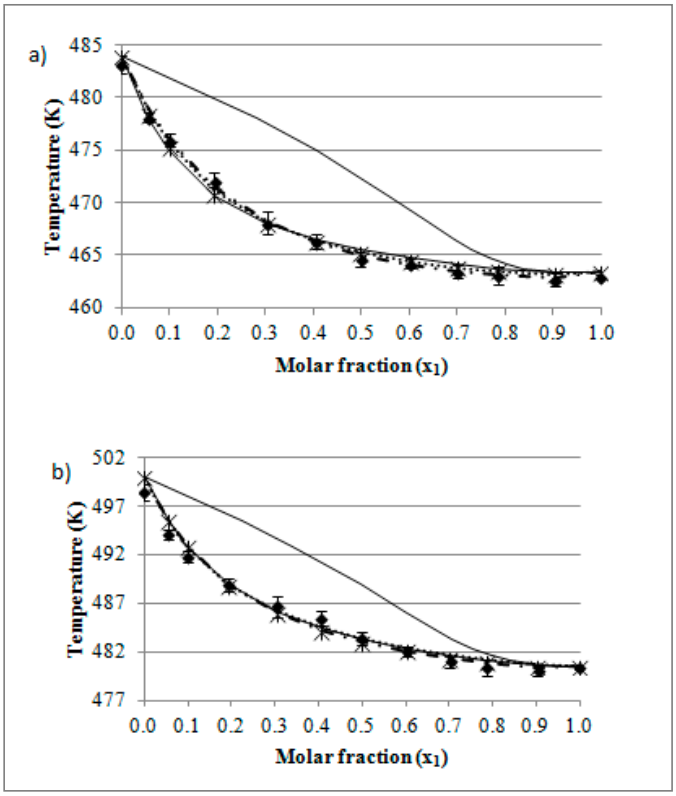

Figure 60: VLE of system 1 [monocaprylin(1) + palmitic acid(2)] at a)1.2 kPa and b)2.5 kPa. ◆Experimental data (this work); — NRTL (with vapour phase calculated by the model); * UNIQUAC; -.-.- Wilson; ••••••• Modified UNIFAC.

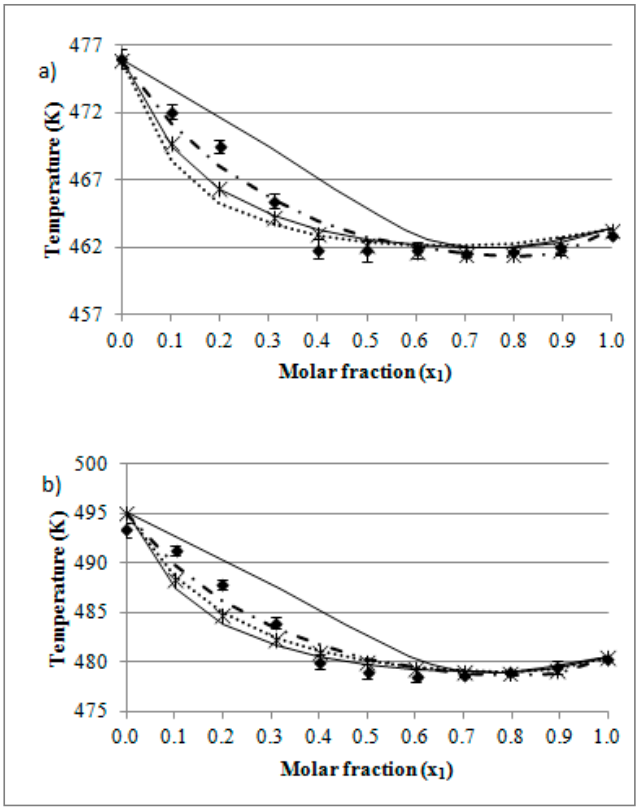

Figure 61: VLE of system 2 [monocaprylin(1) + methyl stearate(2)] at a)1.2 kPa and b)2.5 kPa. ◆Experimental data (this work); — NRTL (with vapour phase calculated by the model); * UNIQUAC; -.-.- Wilson; •••••• Modified UNIFAC.

For system 1, a non-ideal behaviour is observed at both pressures, and the boiling points of the binary mixtures richer in the heaviest compound (palmitic acid) change substantially, that is, for the concentration range of monocaprylin between 0.0 and 0.5. For system 2, non-ideality is even more pronounced at both pressures, and the boiling points of the binary mixtures richer in the heaviest compound (methyl stearate, in this case) decrease substantially, that is, for the concentration of monocaprylin between up 0.0 and 0.4. Otside the range, the boiling points remain almost unchanged (less than 2.0 K of difference among the measured values). It can be noted that both systems form minimum boiling azeotropes, that is, the boiling temperatures of the binary mixtures are lower than the values of the pure components. Non-idealities as the ones observed in this work have also been found by Coelho et al.[9] and Veneral et al. [238], for mixtures

of ethanol and glycerol or ethyl esters, and for mixtures of biodiesel and methanol or ethanol. All of them have shown negative deviations from ideality.One should note that for the DSC technique, deviations lower than 1.3 K among replicates of measured boiling points are considered adequate.

The results found for the thermodynamic consistency tests applied for the measured VLE data in this work are given in Tables 30 and 31 for the variation of the Van Ness test ($Q_{test,1}$ of TDE program developed at NIST [132–138]), and for the pure component consistency test (Qtest,5 of TDE program developed at NIST [132–138]), respectively. For calculating the vapor pressures, Antoine equations are used (Table 32). For the variation of the Van Ness test, only the NRTL model is reported, since Wilson, NRTL and UNIQUAC models gave very similar results for the boiling point calculations (see Tables 33).

It can be noted from Table 30 that the values of the quality factor values (Q_{test1}) are higher than 0.77, wich is an indicative of satisfactory quality of the measured data. Regarding the pure component test (see Table 31), for both systems at the two pressures considered, the quality factors (Q_{test5}) are equal to 1 due the absolute deviation observed for the pressure (Δp_i^0), indicating that the endpoints of the binary mixture analyzed are in agreement with the expected values of the pure components found.

Table 30: Experimental data sets and the quality factors calculated for Van Ness consistency test.

Experimental data sets	Pressure (kPa)	Quality factor (Q_{test1})
Monocaprylin(1) + palmitic acid(2)	1.2	0.893
	2.5	0.861
Monocaprylin(1) + methyl stearate(2)	1.2	0.785
	2.5	0.776

Table 31: Experimental data points (x1 = 0 and x1 = 1) and the necessary variables for the quality factor calculation in the pure component consistency test.

Temperature (K)	Measured values	Pressure (kPa)	From open literature [a]	Pressure (kPa)	Δp_i^0
462.94	$x_1 = 1$	1.2	Monocaprylin	1.1	0.1
480.41		2.5		2.7	0.2
483.15	$x_1 = 0$	1.2	Palmitic acid	1.2	0.0
498.35		2.5		2.3	0.2
475.97	$x_1=0$	1.2	Methyl stearate	1.2	0.0
493.38		2.5		2.3	0.2

[a] CAPEC_Lipids_Database

The regressed parameters for Wilson, NRTL and UNIQUAC models are also given in Table 33. The parameters from Wilson are λ_{12} and λ_{21} in K-1. The values of the molar volume values required by the Wilson model were calculated using Marrero and Gani group contribution method [198], to be 213.32 cm3.mol-1 for monocaprylin, 295.63 cm3.mol-1 for palmitic acid, and 348.35 cm3.mol-1 for methyl stearate. The parameters from NRTL are Δg12 and Δg21 in J.mol-1, and α12. The parameters for the UNIQUAC model are Δu12 and Δu21 in J.mol-1.

Table 32: Parameters for Antoine equations for vapour pressure of compounds.

Compounds	A	B	C
Monocaprylin	24.808	-11522.0	3.692
Palmitic acid	23.372	-11385.9	7.032
Methyl stearate	20.002	-9873.2	22.208

[a] ln Psat/kPa = A+B/(T+C), T in K.

The vapour phase fugacity coefficient were calculated using the "chemical theory" for predicting the second Virial Coefficient [239]. Taking into account the class of the compounds in the binary mixtures (carboxylic acids and glycerol, for example), the association of the compounds via stable hydrogen bonds could lead to large deviation from the ideal behaviour. Nevertheless, the values found for the fugacity coefficients are close to unity, indicating ideal behaviour for vapour phase, which can be explained by the effect of the long carbon chain of the carboxylic acid that makes its dimerization weak or absent [240,241]. Perhaps most importantly, the observed behaviour is a

consequence of the low pressures considered (ideal gas). Same behaviour has been observed by Matricarde Falleiro et al. [170,171] for binary mixtures of fatty acids.

Figures 56 and 57 show the performance for the selected thermodynamic model for systems 1 and 2, respectively. It can be noted that a good representation of experimental results was obtained at both pressures for the selected thermodynamic models (Wilson, NRTL, and UNIQUAC) with ARD lower than 0.3%.

Table 33: Binary interaction parameters for Wilson, NRTL and UNIQUAC models and the experimental data sets.

System	Pressure (kPa)	Temperature rage (K)	Wilson parameters			NRTL parameters				UNIQUAC parameters		
			λ_{12} / K	λ_{21} / K	ARD (%)	Δg_{12}/ J.mol^{-1}	Δg_{21}/ J.mol^{-1}	α_{12}	ARD (%)	Δu_{12}/ J.mol^{-1}	Δu_{21}/ J.mol^{-1}	ARD (%)
Monocaprylin (1) + palmitic acid (2)	1.2	462.94 - 483.15	130.6	891.74	0.101	6304.11	-409.72	0.3	0.120	219.83	219.5	0.225
	2.5	480.41 - 498.35	943.54	-341.7	0.107	1245.42	1261.41	0.3	0.162	101.73	103.01	0.174
Monocaprylin (1) + methyl stearate (2)	1.2	462.94 - 475.97	252.88	562.58	0.190	2723.7	2720.51	0.3	0.274	218.61	233.56	0.190
	2.5	480.41 - 493.38	202.06	132.4	0.265	1345.67	1339.91	0.3	0.289	102.32	101.84	0.271

7.6.1 Modified UNIFAC proposed for the measured data

The original UNIFAC model parameters [17] does not give good predictions. Considering that lipids systems may not have been considered in the databank of the original UNIFAC, a possible way to improve its performance is to fine-tune the group interaction parameters using the lipids datasets. This, in this work, new interaction parameters are regressed for the functional groups, such as the main group COOH for fatty acids with the main group CH2. Main groups used in system 1 are: CH2, CCOO, OH and COOH. In system 2, the same main groups are used except COOH. Since a large number of interaction parameters were necessary for the VLE calculation in comparison with the measured data points, an objective function employing a regularization term [190] F_R was considered. This was also done by Balslev and Abildskov [191]. In this work, the optimal β was 104, and a^0_{mn} was set to the current UNIFAC values. The current and the revised binary interaction parameters for UNIFAC model are given in Table 34. Perhaps not unexpected, the greatest changes have been gound for the hydrocarbon-alcohol interaction parameters. For system 1, ARD values are found to be from 0.37 % for original UNIFAC to 0.33 % for modified UNIFAC, and for system 2 this difference is more substantial, 1.47 % for original UNIFAC and 0.33 % for modified UNIFAC. Also, no phase split is found for system 2. It is important to note that the obtained parameters should be used only for systems covered by the measured data.

Table 34: Binary interaction parameters for original and modified UNIFAC model used in the experimental data sets calculations.

Current UNIFAC matrix				
	CH3/CH2/CH	OH	CH2COO	COOH
CH3/CH2/CH	0	986.5	232.1	663.5
OH	156.4	0	101.1	199
CH2COO	114.8	245.4	0	660.2
COOH	315.3	-151	-256.3	0
Revised UNIFAC matrix				
	CH3/CH2/CH	OH	CH2COO	COOH
CH3/CH2/CH	0.00	391.23	284.80	624.17
OH	-91.60	0.00	19.80	337.67
CH2COO	153.89	180.88	0.00	691.69
COOH	267.97	-28.04	-160.89	0.00

7.6.2 Challenges in the experimental data work procedure

The equipment requires a very careful preparation of mixture samples, considering that only 0.2 g of each binary mixture with a specific molar fraction was prepared and only 4 to 5mg of it is required for performing a thermogram in DSC. Some reagents, as the palmitic acid and monocaprylin, are solid in ambient temperature, which make difficult the handling of pure components and mixtures in the sample preparation. For many times a triplicate was not enough to ensure the quality of a data point. Pressure calibration using a known compound (tetradecane) is the first step before starting a boiling point measurement for the binary mixture.

While performing the thermodynamic consistency analysis, the TDE program does not have one of the compounds (monocaprylin), probably because of the lack of pure component and mixture properties in literature. Even though the program allows the user to add the compound, many properties calculated by the program could not be rejected before the thermodynamic consistency analysis.

The DSC technique for VLE measurements has some limitations, such as the requirement of an interval of boiling point temperatures between the compounds utilized for binary mixtures. If the difference between the two boiling points are too large, the onset temperature cannot be read, as explained by Falleiro [242]. Also the split of the liquid phase cannot be determined considering only DSC technique. Some selected mixtures could not have the measurements performed due these limitations, such as Monostearin and Tricaprylin, or Monocaprylin and Ethyl myristate. Also, one more system (glycerol + monocaprylin) was selected to have the boiling point measured and have the results given in Figure 62 for 1.2 and 2.5KPa. Nevertheless, it was observed an unexpected increase of temperature after the molar fraction of the compound 1 (glycerol) equal 0.2. Due this unexpected behaviour, the stability analysis was performed considering the follow statement [243]:

$$\frac{d\,ln\,\gamma_i}{dx_i} > -\frac{1}{x_i} \tag{38}$$

Where γ_i is the activity coefficient and x_i is the molar fraction of compound i. However, to guarantee the efficiency of the analysis, it is necessary to have a thermodynamic model that could represent the experimental data. In this case, Redlich-Kister equation [244] was selected because it is able to represent experimental data using more than a second order equation. As can be seen in Figure 63, it was found that

one more liquid phase was present and most probably VLLE was given as results from DSC technique. Once the LLE could not be determined because it requires the use of high quantities of monocaprylin (with purity of 99%), for example in visual measurements, this part of the experimental work was not published and is kept for internal research.

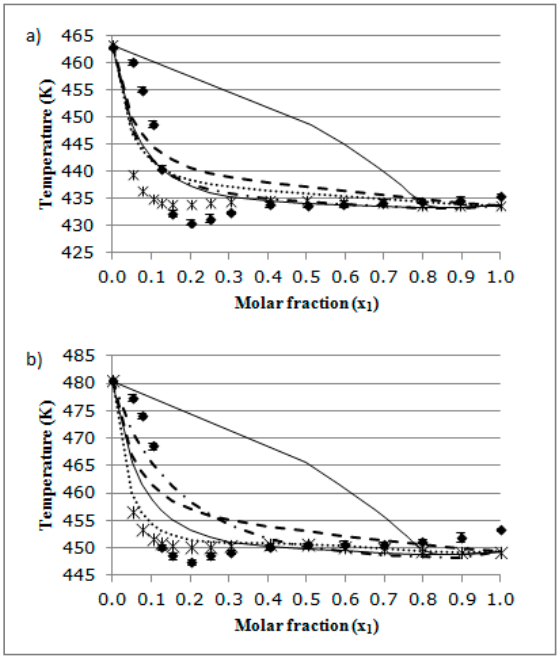

Figure 62: VLE of glycerol(1) + monocaprylin(2) at a)1.2 kPa and b)2.5 kPa. ◆Experimental data (this work); — NRTL (with vapour phase calculated by the model); * UNIQUAC; -.-.- Wilson; ••••••• Modified UNIFAC.

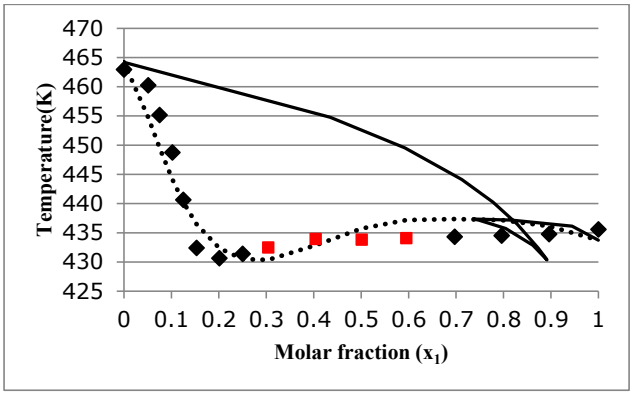

Figure 63: VLE of glycerol (1) + monocaprylin(2) at a)1.2 KPa and b)2.5 KPa. ◆Experimental data (this work); •••••• Redlich Kister expansion; — Calculated vapour phase using Redlich Kister expansion; ■ Data points that did not pass in the stability test.

Chapter 8. Conclusions and future work

The achieviments obtained in this project for modelling of phase equilibria and related properties are:

- Observing the performance for well-known G^E-based models (original UNIFAC, UNIQUAC, NRTL), it is possible to conclude that the NRTL and the UNIQUAC models give similar deviations for the calculated VLE behaviour while the original UNIFAC model generally gives larger deviations, when "general" parameters are used. Note, however, the NRTL and the UNIQUAC model parameters have been fitted to the available data while the original UNIFAC model parameters did not use the same data for their regression. Fine-tuning the model parameters with the same data used for the NRTL or the UNIQUAC, however, results in similar model performance. For SLE systems, the models performances are similar to the VLE calculations.
- CAPEC_Lipids_Database and CAPEC_Lipids_Mixture_Database have been extended with the information of consistent thermodynamic model parameters for GE-based models (NRTL, UNIQUAC and original UNIFAC). The information of such properties and the quality factor for each experimental data set utilizing thermodynamic consistency tests can be seen in the supplementary material. For VLE, it is important to notice the general coefficients for vapour pressure that could be utilized in different references of mixtures containing lipids would be desirable and plays an important role in parameter regression, and this relies in the consistency of the available data. Original UNIFAC model representation can be improved for lipids systems using a specific database for group-contribution parameter regression. Increasing the regularization term value, it is possible to observe better model representation once original UNIFAC model calculated the non-ideality observed in the binary mixtures: hexane and oleic acid, acetone and triolein, and hexane and triolein. Also the problem observed in the unreal prediction of LLE split for some of the data sets was corrected after the parameter regression. The inclusion of a new binary interaction group (OH acyl) for monoacylglycerols has improvement

substantially original UNIFAC model representation for mixtures including these compounds.

- Once obtained new interaction parameters for original UNIFAC that can better represented VLE and SLE data sets containing lipids compounds, the next step was to observe the model performance for LLE data sets. Original UNIFAC parameters have been compared with LLE parameters for data sets containing lipids. The results showed improvement in some of the cases using LLE parameters such for liquid solubility of fatty acids in water.
- PC-SAFT model combined with GC showed improvement in the calculation of pure component properties (vapour pressure, enthalpy of fusion and density) for lipids after fined-tuning the pure component parameters considering only lipids data. Also it could be observed that there is a lack of pure component parameter values for lipids systems and PC-SAFT in literature.
- Accuracy of the measured experimental data is important to guarantee a good performance by predictive thermodynamic models such as original UNIFAC. For VLE systems, it has been observed that a large percentage of reported measured data for lipid systems failed the consistency tests used in this work [133–139].
- The status of property and phase equilibria for lipid systems has been reviewed and advanced by more thorough investigation of SLE and solubility data and their analysis, as well as by using an activity coefficient formulation based on Fluctuation Solution Theory (FST). Though no rigorous consistency tests exist for such systems, using a reliable activity coefficient model along with comparing limits with independent pure compound data allows Quality Factors to be established for complete composition range and limited range solubility SLE. It was found that the FST model is normally more accurate than either the NRTL or UNIQUAC models.
- Exploration of the sensitivity to different objective functions for the regression showed that somewhat different parameter values are obtained, but that the differences in quality of the model descriptions were similar. The same approach adopted here for SLE.

- Iodine values could be calculated for vegetable oils and biodiesel compounds with good agreement with experimental values containing the information of composition of the compounds.
- A novel DSC technique to measure VLE data for monocaprylin with palmitic acid, and monocaprylin with methyl stearate has been employed. The DSC technique is considered suitable for the two binary mixtures studied in this work mainly because of the low amounts of mass used in each sample. Satisfactory results have been obtained from the employed thermodynamic consistency tests, indicating the acceptable quality of the measured VLE data. The model parameters for the Wilson, NRTL and UNIQUAC models have been regressed with the measured data, with ARD(%) lower than 0.3 % for all cases. Also, the Original UNIFAC model with regressed parameters and employing regularization in the objective function, gave satisfactory representation of the VLE data for the two binary systems.

8.1 Suggestions for further work

- The proposed parameters for original UNIFAC model should be also tested in multicomponent systems. In the case where interaction parameters are missing for original UNIFAC model due to the lack of experimental data, for VLE as well as SLE, the UNIFAC-CI method provides an option to predict the needed model parameters when no measured data are available to estimate them.
- Parameter regression considering lipids data can be an option to also improve model performance of original UNIFAC model for LLE data.
- More compounds should be considered in further analysis of PC-SAFT model, once there is only one source of association parameters in literature for lipids. Also the prediction of VLE, SLE and LLE for mixtures involving lipids can be analyzed considering the proposed GC parameters. For mixtures, the need of the association parameters for PC-SAFT model can be one issue to be studied.
- A predictive model based in FST can be developed once it was observed improvement in the model representation of lipid systems, mainly close to composition of the end points (x_1=0 and x_1=1), once FST is a unsymetric model. Regarding the thermodynamic consistency tests, it would be desible to have a

methodology to analyze LLE, systems at high temperature and pressure, and also mixtures containing associative compounds.

- For cloud point, as reported by Hammami et al. [233] for oil, new techniques are necessary to assure reliable experimental measurements, once the precipitation kinetics and solid phase detection limits should also be considered.
- There are still many data missing in literature, for example for acylglycerols, and the same technique utilized for the measured data sets (DSC) could be utilized for more binary or multicomponent mixtures including lipids.

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Appendix 1

Table 1: Binary mixtures database for lipids (CAPEC_Lipids_Database)

Number at the database	BINARY MIXTURE		Experimental data accuracy given by the author(s)	Phase Equilibrium	Thermodynamic models used by the author(s)
	LIPID	Second compound			
1	Pentanoic acid	Water	Yes	Solubility / LLE	CPA-EOS (CR2 and CR4)
2	Hexanoic acid	Water	Yes	Solubility / LLE	CPA-EOS
3	Hexanoic acid	Water	No	Solubility	Just Experimental data
4	Hexanoic acid	Water	Not possible to determine	Solubility	NRTL / UNIQUAC
5	Hexanoic acid	Acetone	Yes	Solubility	Just Experimental data
6	Hexanoic acid	Octanoic acid	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC
7	Hexanoic acid	Octanoic acid	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC
8	Heptanoic acid	Water	Yes	Solubility	CPA-EOS
9	Heptanoic acid	Water	No	Solubility	Just Experimental data
10	Heptanoic acid	Water	No	Solubility	Just Experimental data
11	Octanoic acid	Water	Yes	Solubility	CPA-EOS
12	Octanoic acid	Water	No	Solubility	Just Experimental data

Table 1: Binary mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

13	Octanoic acid	Acetone	Yes	Solubility	Just Experimental data
14	Octanoic acid	Acetone	No	Solubility	Just Experimental data
15	Octanoic acid	Decanoic acid	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC
16	Nonanoic acid	Water	Yes	Solubility	CPA-EOS
17	Nonanoic acid	Water	No	Solubility	Just Experimental data
18	Decanoic acid	Water	Yes	Solubility	CPA-EOS
19	Decanoic acid	Water	No	Solubility	Just Experimental data
20	Decanoic acid	Acetone	Yes	Solubility	Just Experimental data
21	Decanoic acid	Acetone	Yes	Solubility	Just Experimental data
22	Decanoic acid	Lauric acid	Not possible to determine	VLE	Margules / Wilson / NRTL / UNIQUAC
23	Dodecanoic acid	Water	Yes	LLE	CPA-EOS
24	Dodecanoic acid	Water	No	Solubility	Just Experimental data
25	Lauric acid	Myristic acid	Yes	SLE	Just experimental data
26	Lauric acid	Myristic acid	No	SLE	Margules 2suf / NRTL
27	Lauric acid	Myristic acid	Yes	SLE	Margules 3suf / UNIFAC
28	Lauric acid	Myristic acid	Yes	SLE	Just experimental data
29	Lauric acid	Myristic acid	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC

Table 1: Binary mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

30	Lauric acid	Myristic acid	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC
31	Lauric acid	Myristic acid	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC
32	Lauric acid	Myristic acid	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC
33	Lauric acid	Hexane	Yes	Solubility	Wilson / NRTL / UNIQUAC
34	Lauric acid	Acetone	Yes	Solubility	Wilson / NRTL / UNIQUAC
35	Lauric acid	Acetone	No	Solubility	Just experimental data
36	Lauric acid	Acetone	No	Solubility	Just experimental data
37	Lauric acid	Acetone	No	Solubility	Just experimental data
38	Lauric acid	Palmitic acid	No	SLE	Margules 2suf / NRTL
39	Lauric acid	Palmitic acid	Yes	SLE	Margules 3suf / UNIFAC
40	Lauric acid	Stearic acid	No	SLE	Margules 2suf / NRTL
41	Lauric acid	Stearic acid	Yes	SLE	Margules 3suf / UNIFAC
42	Lauric acid	Stearic acid	Yes	SLE	Just experimental data
43	Myristic acid	Palmitic acid	Yes	SLE	Just experimental data
44	Mirystic acid	Palmitic acid	Yes	SLE	Just experimental data

Table 1: Binary mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

45	Myristic acid	Palmitic acid	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC
46	Myristic acid	Palmitic acid	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC
47	Myristic acid	Stearic acid	Yes	VLE	Wilson / NRTL / UNIQUAC
48	Myristic acid	Stearic acid	No	SLE	Margules 2suf / NRTL
49	Myristic acid	Stearic acid	No	SLE	Just experimental data
50	Myristic acid	Water	No	Solubility	Just experimental data
51	Myristic acid	Acetone	No	Solubility	Just experimental data
52	Myristic acid	Acetone	No	Solubility	Just experimental data
53	Myristic acid	Acetone	No	Solubility	Just experimental data
54	Palmitic acid	Stearic acid	Yes	VLE	Wilson / NRTL / UNIQUAC
55	Palmitic acid	Stearic acid	Yes	SLE	Just experimental data
56	Palmitic acid	Stearic acid	Yes	SLE	Margules 2suf / NRTL
57	Palmitic acid	Stearic acid	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC
58	Palmitic acid	Stearic acid	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC
59	Palmitic acid	Acetone	Yes	Solubility	Wilson / NRTL / UNIQUAC
60	Palmitic acid	Acetone	No	Solubility	Just experimental data

Table 1: Binary mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

61	Palmitic acid	Acetone	No	Solubility	Just experimental data
62	Palmitic acid	Acetone	No	Solubility	Just experimental data
63	Palmitic acid	Water	No	Solubility	Just experimental data
64	Palmitic acid	Hexane	Yes	Solubility	Wilson / NRTL / UNIQUAC
65	Myristic acid	Stearic acid	Yes	VLE	Wilson / NRTL / UNIQUAC
66	Palmitic acid	Linoleic acid	Yes	SLE	UNIFAC
67	Stearic acid	Oleic acid	Yes	SLE	Just experimental data
68	Stearic acid	Hexane	Yes	Solubility	Van Laar / Wilson / NRTL / UNIQUAC
69	Stearic acid	Acetone	Yes	Solubility	Van Laar / Wilson / NRTL / UNIQUAC
70	Stearic acid	Acetone	Yes	Solubility	Apelblat equation and Buchowski equation
71	Stearic acid	Acetone	No	Solubility	Just experimental data
72	Stearic acid	Acetone	No	Solubility	Just experimental data
73	Stearic acid	Acetone	No	Solubility	Just experimental data
74	Stearic acid	Acetone	Yes	SLE	Margules / Wilson / NRTL / UNIQUAC
75	Stearic acid	Water	No	Solubility	Just experimental data
76	Oleic acid	Linoleic acid	No	SLE	Just experimental data

Table 1: Binary mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

77	Oleic acid	Acetone	No	Solubility	Just experimental data
78	Oleic acid	Acetone	No	Solubility	Just experimental data
79	Oleic acid	Hexane	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC
80	Oleic acid	Palmitic acid	Yes	SLE	UNIFAC
81	Oleic acid	Palmitic acid	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC
82	Oleic acid	Palmitic acid	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC
83	Linoleic acid	Acetone	No	Solubility	Just experimental data
84	Linoleic acid	Acetone	No	Solubility	Just experimental data
85	Linoleic acid	Acetone	No	Solubility	Just experimental data
86	Arachidic acid	Acetone	No	Solubility	Just experimental data
87	Arachidic acid	Acetone	No	Solubility	Just experimental data
88	Monocaprin ester	Squalene	Yes	Solubility	Just experimental data
89	Monolaurin ester	Squalene	Yes	Solubility	Just experimental data
90	diglycerol monocaprilate	Water	Yes	LLE	Just experimental data
91	diglycerol monolaurate	Water	Yes	LLE	Just experimental data
92	diglycerol monomyristate	Water	Yes	LLE	Just experimental data

Table 1: Binary mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

93	diglycerol monopalmitate	Water	Yes	LLE	Just experimental data
94	Tricaprylin	Acetone	Yes	Solubility	Just experimental data
95	Tricaprin	Acetone	Yes	Solubility	Just experimental data
96	Trilaurin	Acetone	Yes	Solubility	Just experimental data
97	Trimyristin	Acetone	Yes	Solubility	Just experimental data
98	Tripalmitin	1,3-dihexadecanoyl-2-octadecenoyl-sn-glycerol	Not possible to determine	SLE	Margules
99	Tripalmitin	Triolein	Yes	SLE	Just experimental data
100	Tripalmitin	Triolein	Yes	SLE	Margules3suf / Margules2suf / NRTL / UNIFAC
101	Tripalmitin	Triolein	Yes	SLE	UNIFAC
102	Tripalmitin	Oleic acid	Yes	SLE	UNIFAC
103	Tripalmitin	Oleic acid	Yes	SLE	Just experimental data
104	Tripalmitin	Oleic acid	Yes	SLE	UNIFAC
105	Tripalmitin	Linoleic acid	Yes	SLE	UNIFAC
106	1,3-dihexadecanoyl-2-octadecanoyl-sn-glycerol	Tripalmitin	Not possible to determine	SLE	Just experimental data

Table 1: Binary mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

107	1,3-dihexadecanoyl-2-octadecanoyl-sn-glycerol	1,3-dioctadecanoyl-2-dihexadecanoyl-sn-glycerol	No	SLE	Just experimental data
108	1,3-dihexadecanoyl-2-octadecenoyl-sn-glycerol	1,3-dioctadecenoyl-2-hexadecanoyl-sn-glycerol	No	SLE	Just experimental data
109	1,3-dihexadecanoyl-2-octadecenoyl-sn-glycerol	1,2-dioctadecenoyl-3-hexadecanoyl-sn-glycerol	No	SLE	Just experimental data
110	1,2-dihexadecanoyl-3-octadecenoyl-sn-glycerol	1,3-dihexadecanoyl-2-octadecenoyl-sn-glycerol	No	SLE	Just experimental data
111	1-hexadecanoyl-2-octadecanoyl-3-octadecenoyl-sn-glycerol	1,3-dioctadecanoyl-2-octadecenoyl-sn-glycerol	No	SLE	Just experimental data
112	1-hexadecanoyl-2,3-dioctadecenoyl-sn-glycerol	Tripalmitin	Not possible to determine	SLE	Just experimental data
113	Triolein	Palmitic acid	Yes	SLE	UNIFAC-DMD
114	Triolein	Palmitic acid	Yes	SLE	UNIFAC
115	Triolein	Palmitic acid	Yes	SLE	Just Experimental data
116	Triolein	Acetone	Yes	Solubility	Just experimental data
117	Triolein	Methanol	Yes	VLE	SRK / PR / RK-ASPEN EOS
118	Triolein	Methanol	Yes	VLE	Just experimental data
119	Trilinolein	Acetone	Yes	Solubility	Just experimental data

Table 1: Binary mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

120	Methyl hexanoate	Water	Yes	Solubility	UNIFAC / SRK / PSRK / PR-MHV2 / SRK-MHV2 / CPA
121	Methyl hexanoate	Acetone	Yes	Solubility	Just Experimental Data
122	Methyl heptanoate	Water	Yes	Solubility	UNIFAC / SRK / PSRK / PR-MHV2 / SRK-MHV2 / CPA
123	Methyl octonoate	Water	Yes	Solubility	UNIFAC / UNIFAC-LL / UNIFAC-DMD
124	Methyl octanoate	Water	Yes	Solubility	UNIFAC / SRK / PSRK / PR-MHV2 / SRK-MHV2 / CPA
125	Methyl octanoate	Acetone	Yes	Solubility	Just Experimental Data
126	Methyl decanoate	Acetone	Yes	Solubility	Just Experimental Data
127	Methyl dodecanoate	Water	Yes	Solubility	UNIFAC / SRK / PSRK / PR-MHV2 / SRK-MHV2 / CPA
128	Methyl Laurate	Methanol	No	VLE	PR -Stryjek–Vera with PRASOG mix. Rule
129	Methyl Laurate	Methanol	Yes	VLE	CPA-EOS
130	Methyl Laurate	Ethanol	Yes	VLE	CPA-EOS
131	Methyl Laurate	Methyl Myristate	Yes	VLE	Just experimental data
132	Methyl Laurate	Methyl stearate	Yes	SLE	Predictive UNIQUAC
133	Methyl Laurate	Lauric acid	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC

Table 1: Binary mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

134	Methyl Laurate	Acetone	Yes	Solubility	Just Experimental Data
135	Methyl tetradecanoate	Water	Yes	Solubility	UNIFAC / SRK / PSRK / PR-MHV2 / SRK-MHV2 / CPA
136	Methyl Myristate	Methanol	No	VLE	PR -Stryjek–Vera with PRASOG mix. Rule
137	Methyl Myristate	Methanol	Yes	VLE	CPA-EOS
138	Methyl Myristate	Ethanol	Yes	VLE	CPA-EOS
139	Methyl myristate	Methyl pamitate	No	SLE	Just experimental data
140	Methyl myristate	Methyl pamitate	Yes	VLE	Wilson / NRTL / UNIQUAC
141	Methyl myristate	Methyl pamitate	Yes	VLE	Just experimental data
142	Methyl myristate	Methyl pamitate	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC
143	Methyl myristate	Acetone	Yes	Solubility	Just Experimental Data
144	Methyl hexadecanoate	Water	Yes	Solubility	UNIFAC / SRK / PSRK / PR-MHV2 / SRK-MHV2 / CPA
145	Methyl palmitate	Water	No	Solubility	UNIFAC / UNIFAC-LL / UNIFAC-DMD
146	Methyl palmitate	Acetone	Yes	Solubility	Just Experimental Data
147	Methyl palmitate	Methyl stearate	Yes	SLE	Predictive UNIQUAC
148	Methyl palmitate	Methyl stearate	No	SLE	Just experimental data
149	Methyl palmitate	Methyl stearate	Yes	VLE	Just experimental data

Table 1: Binary mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

150	Methyl palmitate	Methyl stearate	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC
151	Methyl palmitate	Methyl linoleate	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC
152	Methyl octadecanoate	Water	Yes	Solubility	UNIFAC / SRK / PSRK / PR-MHV2 / SRK-MHV2 / CPA
153	Methyl stearate	Hexane	Yes	VLE	Margules / Wilson / NRTL / UNIQUAC
154	Methyl stearate	Acetone	Yes	VLE	Margules / Wilson / NRTL / UNIQUAC
155	Methyl stearate	Acetone	Yes	Solubility	Just Experimental Data
156	Methyl stearate	Methyl myristate	No	SLE	Just experimental data
157	Methyl Oleate	Methyl stearate	Not possible to determine	VLE	Just Experimental Data
158	Methyl Oleate	Methanol	No	VLE	GC-PPC-SAFT
159	Methyl Oleate	Methanol	No	LLE	GC-PPC-SAFT
160	Methyl Oleate	Methanol	Yes	VLE	CPA-EOS and GC-PPC-SAFT by other authors
161	Methyl Oleate	Ethanol	Yes	VLE	CPA-EOS
162	Methyl oleate	Water	Yes	Solubility	UNIFAC / SRK / PSRK / PR-MHV2 / SRK-MHV2 / CPA
163	Methyl oleate	Water	No	Solubility	UNIFAC / UNIFAC-LL / UNIFAC-DMD
164	Methyl oleate	Acetone	Yes	Solubility	Just Experimental Data

Table 1: Binary mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

165	Methyl oleate	Methyl stearate	Yes	SLE	Predictive UNIQUAC
166	Methyl linoleate	Methyl stearate	Yes	SLE	Predictive UNIQUAC
167	Ethyl decanoate	Water	Yes	Solubility	UNIFAC / SRK / PSRK / PR-MHV2 / SRK-MHV2 / CPA
168	Ethyl Laurate	Ethanol	No	VLE	PR -Stryjek–Vera with conversional mix. Rule and WS
169	Ethyl laurate	Ethyl Palmitate	Yes	SLE	Predictive UNIQUAC
170	Ethyl myristate	Ethyl Palmitate	Yes	SLE	Predictive UNIQUAC
171	Ethyl myristate	Ethyl stearate	Yes	SLE	Predictive UNIQUAC
172	Ethyl myristate	Ethanol	No	VLE	PR -Stryjek–Vera with conversional mix. Rule and WS
173	Ethyl Palmitate	Ethanol	Yes	VLE	NRTL / UNIQUAC / UNIFAC / UNIFAC - Dortmund
174	Ethyl palmitate	Ethyl stearate	Yes	VLE	Wilson / NRTL / UNIQUAC
175	Ethyl Palmitate	Ethyl oleate	Yes	SLE	Predictive UNIQUAC
176	Ethyl Palmitate	Ethyl oleate	Yes	VLE	Wilson / NRTL / UNIQUAC
177	Ethyl Stearate	Ethanol	Yes	VLE	NRTL / UNIQUAC / UNIFAC / UNIFAC - Dortmund
178	Ethyl stearate	Ethyl laurate	Yes	SLE	Predictive UNIQUAC
181	Ethyl linoleate	Ethyl stearate	Yes	SLE	Predictive UNIQUAC
182	Ethyl linoleate	Ethyl Palmitate	Yes	SLE	Predictive UNIQUAC

Table 1: Binary mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

183	Ethyl linoleate	Ethyl Palmitate	Yes	VLE	Wilson / NRTL / UNIQUAC
184	Cottonseed Oil	Hexane	Yes	VLE	UNIFAC / UNIFAC-SGr3/4 / UNIFAC-FV / UNIFAC-ELBRO
185	Soybean Oil	Hexane	Yes	VLE	Just Experimental Data
186	Canola Oil	Ethanol	Yes	LLE	NRTL
187	Corn Oil	Ethanol	Yes	LLE	NRTL
188	Soybean Biodiesel	Methanol	Yes	LLE	Wilson and modelling by other authors using UNIFAC / UNIFAC-LLE / UNIFAC-DMD
189	Sunflower Biodiesel	Ethanol	No	VLE	Just experimental
190	Palm Oil Biodiesel	Glycerol	Yes	Solubility	Just experimental data
191	Glycerol	Water	Yes	VLE	NRTL / UNIQUAC / UNIFAC / UNIFAC - Dortmund
192	Glycerol	Water	Yes	VLE	CPA-EOS
193	Glycerol	Water	Yes	VLE	Just experimental data
194	Glycerol	Water	Yes	VLE	Wilson
195	Glycerol	Water	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC
196	Glycerol	Water	Not possible to determine	VLE	Margules / Van Laar / Wilson / NRTL / UNIQUAC

Table 1: Binary mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

197	Glycerol	Ethanol	Yes	VLE	NRTL / UNIQUAC / UNIFAC / UNIFAC - Dortmund
198	Glycerol	Ethanol	Yes	VLE	PR -Stryjek–Vera with conversional mix. Rule and PRASOG model
199	Glycerol	Ethanol	Yes	VLE	CPA-EOS
200	Glycerol	Methanol	No	VLE	GC-PPC-SAFT
201	Glycerol	Methanol	Yes	VLE	PR -Stryjek–Vera with conversional mix. Rule and PRASOG model
202	Glycerol	Methanol	Yes	VLE	CPA-EOS and GC-PPC-SAFT by other authors
203	Glycerol	Methanol	Yes	LLE	Wilson
204	Glycerol	Methanol	Yes	LLE	Wilson
205	Tocopherol	Methanol	Yes	VLE	PR-EOS (High pressure and temperature)
206	Tocopherol	CO2	Yes	VLE	PR-EOS (High pressure and temperature)

Table 2: Ternary and multicompent mixtures database for lipids (CAPEC_Lipids_Database)

Number at the database	LIPID	MULTICOMPONENT MIXTURES					Experimental data accuracy	Phase Equilibrium	Thermodynamic models used by the authors
		Second compound	Third compound	Forth compound	Fifth compound	Sixth compound			
207	Pentanoic acid	Methanol	Water	-	-	-	Not possible to determine	VLE	Just Experimental Data
208	Octanoic acid	Methanol	Water	-	-	-	Not possible to determine	VLE	Just Experimental Data
209	Lauric acid	Myristic acid	Ethanol	-	-	-	Yes	SLE / Solubility	NRTL
210	Lauric acid	Myristic acid	Acetone	-	-	-	Yes	SLE / Solubility	NRTL
211	Lauric acid	Myristic acid	Acetone	Water	-	-	Yes	SLE / Solubility / Binodal data	NRTL
212	Lauric acid	Myristic acid	Ethanol	Water	-	-	Yes	SLE / Solubility / Binodal data	NRTL
213	Lauric acid	Ethanol	Water	-	-	-	Yes	SLE/ Binodal data	NRTL / UNIFAC
214	Lauric acid	Acetone	Water	-	-	-	Yes	SLE/ Binodal data	NRTL / UNIFAC
215	Myristic acid	Ethanol	Water	-	-	-	Yes	SLE/ Binodal data	NRTL / UNIFAC
216	Myristic acid	Acetone	Water	-	-	-	Yes	SLE/ Binodal data	NRTL / UNIFAC

Table 2: Ternary and multicompent mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

217	Palmitic acid	Ethanol	Water	-	-	-	Yes	SLE/ Binodal data	NRTL / UNIFAC
218	Palmitic acid	Acetone	Water	-	-	-	Yes	SLE/ Binodal data	NRTL / UNIFAC
219	Palmitic acid	Methanol	Glycerol	-	-	-	No	LLE	UNIFAC
220	Palmitic acid	Acetone	Hexane	-	-	-	Yes	Solubility	NIBS/ Redlich-Kister model
221	Stearic acid	Methanol	Glycerol	-	-	-	No	LLE	UNIFAC
222	Oleic Acid	Ethanol	Water	-	-	-	Yes	LLE	NRTL
223	Oleic Acid	Methanol	Glycerol	-	-	-	No	LLE	UNIFAC
224	Triolein	Stearic acid	Ethanol	-	-	-	Yes	LLE	UNIFAC / ASOG
225	Triolein	Oleic Acid	Ethanol	-	-	-	Yes	LLE	UNIFAC / ASOG
226	Triolein	Oleic Acid	Ethanol	Water	-	-	Yes	LLE	UNIFAC
227	Tricaprilin	Capric Acid	Ethanol	Water	-	-	Yes	LLE	UNIFAC
228	Tricaprilin	Lauric Acid	Ethanol	Water	-	-	Yes	LLE	UNIFAC
229	Tricaprilin	Oleic Acid	Ethanol	Water	-	-	Yes	LLE	UNIFAC
230	Tricaprilin	Linolenic acid	Ethanol	Water	-	-	Yes	LLE	UNIFAC
231	Methyl Oleate	Methanol	Water	-	-	-	Yes	LLE	UNIFAC / UNIFAC-LLE / UNIFAC-DMD / UNIQUAC / NRTL
232	Methyl Oleate	Glycerol	Methanol	-	-	-	No	LLE	Just experimental data

Table 2: Ternary and multicompent mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

233	Methyl Oleate	Glycerol	Methanol	-	-	-	No	LLE / VLLE	GCA-EOS / A-UNIFAC CPA by other authors
234	Methyl Oleate	Methanol	Glycerol				Yes	LLE	UNIFAC / UNIFAC-LLE / UNIFAC-DMD / UNIQUAC / NRTL
235	Methyl Oleate	Methanol	Glycerol	-	-	-	No	VLLE	GC-PPC-SAFT
236	Methyl Oleate	Methanol	Glycerol	-	-	-	Yes	LLE	UNIFAC - Dortmund / UNIFAC
237	Methyl Oleate	Monoolein	Glycerol	-	-	-	Yes	LLE	UNIFAC - Dortmund / UNIFAC
238	Methyl Oleate	Methanol	Glycerol	Water	-	-	Yes	LLE	Wilson
239	Methyl Oleate	Methanol	Glycerol	Water	-	-	No	LLE	Just experimental data
240	Methyl Oleate	Methanol	Glycerol	Hexane	-	-	Yes	LLE	UNIFAC / Modified UNIFAC
241	Methyl Oleate	Oleic acid	Methanol	Water	-	-	No	LLE	UNIQUAC
242	Methyl Oleate	Methanol	Glycerol	Hexane	-	-	No	LLE	Just experimental data
243	Methyl Oleate	Glycerol	Hexane	Water	-	-	No	LLE	Just experimental data
244	Methyl Oleate	Methanol	Glycerol	Hexane	Water	-	No	LLE	Just experimental data

Table 2: Ternary and multicompent mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

245	Methyl Linoleate	Methanol	Water	-	-	-	Yes	LLE	UNIFAC / UNIFAC-LLE / UNIFAC-DMD / UNIQUAC / NRTL
246	Methyl Linoleate	Methanol	Glycerol	-	-	-	Yes	LLE	UNIFAC / UNIFAC-LL / UNIFAC-DMD / UNIQUAC / NRTL
247	FAME 18	Methanol	Tocopherol	-	-	-	Yes	VLE	PR-EOS
248	Methyl Palmitate	Methyl Oleate	Methyl Stearate	Sterols	-	-	Yes	VLE	Just experimental
249	FAMES	Methanol	Tocopherol	Squalene	Sterols		Yes	VLE	Just experimental
250	Ethyl Laurate	Ethanol	Water	-	-	-	Yes	LLE	CPA-EOS
251	Ethyl Myristate	Ethanol	Water	-	-	-	Yes	LLE	CPA-EOS
252	Ethyl Stearate	Ethanol	Glycerol	-	-	-	No	LLE	NRTL / UNIQUAC / UNIFAC-LL
253	Palm Oil	Ethanol	Hexane	-	-	-	Yes	LLE	NRTL
254	Palm Oil	Oleic acid	Ethanol	Water	-	-	Yes	LLE	NRTL
255	Palm Oil	Oleic acid	Ethanol	Water	-	-	Yes	LLE	NRTL / UNIQUAC
256	Palm Oil	Palmitic Acid	Ethanol	-	-	-	Yes	LLE	NRTL / UNIQUAC
257	Palm Oil	Oleic Acid	Ethanol	-	-	-	Yes	LLE	NRTL / UNIQUAC

Table 2: Ternary and multicompent mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

258	Palm Oil	FFA	Ethanol	Water	-	-	Yes	LLE	NRTL / UNIQUAC
259	Palm Oil	Palmitic Acid	Ethanol	Water	-	-	Yes	LLE	NRTL / UNIQUAC
260	Palm Oil	Palmitic Acid	Oleic acid	Ethanol	Water	Carotenoids	Yes	LLE	UNIQUAC
261	Palm Oil	Palmitic Acid	Oleic acid	Ethanol	Water	Tocopherols	Yes	LLE	UNIQUAC
262	Palm Stearin	Palmitic Acid	Ethanol	Water	-	-	Yes	LLE	NRTL
263	Canola Oil	Ethanol	Water	-	-	-	Yes	LLE	NRTL
264	Canola Oil	Ethanol	Hexane	-	-	-	Yes	LLE	NRTL
265	Canola Oil	Ethanol	Hexane	-	-	-	Yes	LLE	NRTL
266	Canola Oil	Oleic acid	Methanol	-	-	-	Yes	LLE	NRTL / UNIQUAC
267	Canola Oil	Oleic acid	Ethanol	-	-	-	Yes	LLE	NRTL / UNIQUAC
268	Canola Oil	Oleic Acid	Ethanol	-	-	-	Yes	LLE	Just experimental data
269	Canola Oil	Oleic Acid	Isopropanol	-	-	-	Yes	LLE	NRTL / UNIQUAC
270	Canola Oil	Oleic Acid	Ethanol	Water	-	-	Yes	LLE	NRTL / UNIQUAC
271	Rapeseed Oil	M Ester	Methanol	-	-	-	No	LLE	Just experimental data
272	Canola Oil	Oleic acid	Ethanol	-	-	-	Yes	LLE	UNIFAC / ASOG

Table 2: Ternary and multicompent mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

273	Corn Oil	Oleic acid	Ethanol	-	-	-	Yes	LLE	UNIQUAC
274	Corn Oil	Oleic acid	Methanol	-	-	-	Yes	LLE	UNIQUAC
275	Corn Oil	Ethanol	Water	-	-	-	Yes	LLE	NRTL
276	Corn Oil	Ethanol	Hexane	-	-	-	Yes	LLE	NRTL
277	Soybean Oil	Ethanol	Hexane	-	-	-	Yes	LLE	NRTL
278	Soybean Oil	Ethanol	Hexane	-	-	-	Yes	LLE	NRTL
279	Soybean Oil	Linolenic acid	Ethanol	-	-	-	Yes	LLE	NRTL
280	Soybean Oil	Linolenic acid	Ethanol	-	-	-	No	LLE	NRTL
281	Soybean Oil	Linolenic acid	Ethanol	Hexane	-	-	Yes	LLE	NRTL
282	Soybean Oil	Linolenic acid	Ethanol	Water	-	-	Yes	LLE	NRTL
283	Soybean Oil	Linolenic acid	Ethanol	Water	-	-	Yes	LLE	NRTL
284	Soybean Oil	Linolenic acid	Ethanol	Water	-	-	No	LLE	NRTL
285	Soybean Oil	Oleic acid	Ethanol	Water	-	-	Yes	LLE	UNIQUAC
286	Sunflower Oil	Oleic acid	Methanol	-	-	-	Yes	LLE	UNIQUAC
287	Sunflower Oil	Oleic acid	Ethanol	-	-	-	Yes	LLE	UNIQUAC
288	Sunflower Oil	FFA	Ethanol	Water	-	-	Yes	LLE	UNIQUAC
289	Sunflower Oil	Oleic acid	Linolenic acid	Ethanol	Water	-	Yes	LLE	NRTL / UNIQUAC

Table 2: Ternary and multicompent mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

290	Cottonseed Oil	Linolenic acid	Ethanol	-	-	-	Yes	LLE	NRTL / UNIQUAC
291	Cottonseed Oil	Linolenic acid	Ethanol	-	-	-	Yes	LLE	Just experimental
292	Cottonseed Oil	Ethanol	Hexane	-	-	-	Yes	LLE	NRTL
293	Cottonseed Oil	Ethanol	Water	-	-	-	Yes	LLE	Just experimental
294	Cottonseed Oil	Linolenic acid	Ethanol	Water	-	-	Yes	LLE	NRTL / UNIQUAC
295	Cottonseed Oil	Linolenic acid	Ethanol	Water	Tocopherols		Yes	LLE	NRTL / UNIQUAC
296	Rapeseed Oil	Methanol	Water	-	-	-	Yes	LLE	Just experimental data
297	Palm Biodiesel	Methanol	Glycerol	Water	-	-	No	LLE	Wilson
298	Soybean Biodiesel	Glycerol	Ethanol	-	-	-	Yes	LLE	NRTL
299	Soybean Biodiesel	Glycerol	Ethanol	-	-	-	Yes	LLE	Just experimental data
300	Soybean Biodiesel	Ethanol	Water	-	-	-	Yes	LLE	Just experimental data
301	Soybean Biodiesel	Glycerol	Methanol	-	-	-	Yes	LLE	Just experimental data
302	Soybean Biodiesel	Soybean Oil	Ethanol	-	-	-	Yes	LLE	Just experimental data

Table 2: Ternary and multicompent mixtures database for lipids (CAPEC_Lipids_Database) **(Continuation)**

303	Soybean Biodiesel	Ethanol	Glycerol	-	-	-	Yes	LLE	Just experimental data
304	Canola Biodiesel	Glycerol	Ethanol	-	-	-	Yes	LLE	CPA-EOS
305	Sunflower Biodiesel	Glycerol	Ethanol	-	-	-	Yes	LLE	NRTL
306	Sunflower Biodiesel	Glycerol	Ethanol	-	-	-	Not possible to determine	VLE	Just experimental data

Appendix 2

Table 1: Thermodynamic model parameters for VLE data and systems involving lipids.

BINARY MIXTURE			UNIQUAC MODEL		NRTL MODEL					UNIFAC MODEL			
LIPID	Second compound	Isob. P (kPa)	u12-u22 (J/mol)	u21-u11 (J/mol)	g12-g22 (J/mol)	g21-g11 (J/mol)	a_{12}	a12	a21	a13	a31	a23	a32
Lauric acid	Myristic acid	0.533	-1174.6858	1125.4807	-2542.0463	945.5197	0.3	-6659.9548	-6922.0589	-	-	-	-
Lauric acid	Myristic acid	0.53	-1298.1821	1260.3480	-1485.1559	-549.0091	0.3	-8846.4487	-11394.3476	-	-	-	-
Lauric acid	Myristic acid	0.5	-1111.5713	1065.2580	-4363.5823	4024.3273	0.3	-4706.6649	-9619.7915	-	-	-	-
		6.7	2530.6980	-1675.0487	5712.0795	-2398.3443	0.3	4820.7792	4839.6754	-	-	-	-
Lauric acid	Myristic acid	1.3	1986.0692	-1557.4864	5118.8369	-3549.5418	0.3	3021.9733	1970.2622	-	-	-	-
		0.4	437.4553	-423.4942	1122.6364	-1129.8989	0.3	5688.2592	5786.2320	-	-	-	-
		6.7	3439.8171	-2219.2894	9409.5038	-4221.8782	0.3	5366.4901	5467.7623	-	-	-	-
Myristic acid	Palmitic acid	1.3	-182.3357	168.8202	4958.7208	-3684.8318	0.3	5184.1837	5275.9888	-	-	-	-
		0.4	-0.0447	11.7549	-1650.5227	1942.2209	0.3	9749.5745	9991.9005	-	-	-	-
Myristic acid	Palmitic acid	0.5	1220.7348	-1201.1530	3893.3325	-4189.8049	0.3	-101309.3410	-101437.9451	-	-	-	-
Myristic acid	Palmitic acid	6.6	72.2798	-68.7544	-116.7401	110.0884	0.3	754.2925	4189.7937	-	-	-	-
Myristic acid	Stearic acid	6.6	-1622.6934	1536.2124	-6628.8939	5099.1585	0.3	-8129.1203	-13235.6443	-	-	-	-
Palmitic acid	Stearic acid	6.6	-4102.5101	3529.8931	-859.4235	-859.4257	0.3	-12522.5103	-12779.9827	-	-	-	-

Appendix 2

Table 1: Thermodynamic model parameters for VLE data and systems involving lipids.

BINARY MIXTURE			UNIQUAC MODEL		NRTL MODEL					UNIFAC MODEL			
LIPID	Second compound	Isob. P (kPa)	u12-u22 (J/mol)	u21-u11 (J/mol)	g12-g22 (J/mol)	g21-g11 (J/mol)	a_{12}	a12	a21	a13	a31	a23	a32
Lauric acid	Myristic acid	0.533	-1174.6858	1125.4807	-2542.0463	945.5197	0.3	-6659.9548	-6922.0589	-	-	-	-
Lauric acid	Myristic acid	0.53	-1298.1821	1260.3480	-1485.1559	-549.0091	0.3	-8846.4487	-11394.3476	-	-	-	-
Lauric acid	Myristic acid	0.5	-1111.5713	1065.2580	-4363.5823	4024.3273	0.3	-4706.6649	-9619.7915	-	-	-	-
		6.7	2530.6980	-1675.0487	5712.0795	-2398.3443	0.3	4820.7792	4839.6754	-	-	-	-
Lauric acid	Myristic acid	1.3	1986.0692	-1557.4864	5118.8369	-3549.5418	0.3	3021.9733	1970.2622	-	-	-	-
		0.4	437.4553	-423.4942	1122.6364	-1129.8989	0.3	5688.2592	5786.2320	-	-	-	-
		6.7	3439.8171	-2219.2894	9409.5038	-4221.8782	0.3	5366.4901	5467.7623	-	-	-	-
Myristic acid	Palmitic acid	1.3	-182.3357	168.8202	4958.7208	-3684.8318	0.3	5184.1837	5275.9888	-	-	-	-
		0.4	-0.0447	11.7549	-1650.5227	1942.2209	0.3	9749.5745	9991.9005	-	-	-	-
Myristic acid	Palmitic acid	0.5	1220.7348	-1201.1530	3893.3325	-4189.8049	0.3	-101309.3410	-101437.9451	-	-	-	-
Myristic acid	Palmitic acid	6.6	72.2798	-68.7544	-116.7401	110.0884	0.3	754.2925	4189.7937	-	-	-	-
Myristic acid	Stearic acid	6.6	-1622.6934	1536.2124	-6628.8939	5099.1585	0.3	-8129.1203	-13235.6443	-	-	-	-
Palmitic acid	Stearic acid	6.6	-4102.5101	3529.8931	-859.4235	-859.4257	0.3	-12522.5103	-12779.9827	-	-	-	-

Table 1: Thermodynamic model parameters for VLE data and systems involving lipids. **(Continuation)**

Palmitic acid	Stearic acid	0.5	-957.6856	928.4696	-3807.5956	3258.7802	0.3	-43440.1443	-43625.7443	-	-	-	-
Palmitic acid	Stearic acid	0.67	6104.3915	-2956.5189	39228.2868	435.2842	0.3	5403.5051	6442.8301	-	-	-	-
Oleic acid	Palmitic acid	0.33	2515.9652	-2488.5046	7856.6344	-9918.6412	0.3	-5418.4625	-1040.7155	-21.5063	57.5147	-1066.7547	-113.4861
Oleic acid	Palmitic acid	0.67	-3605.6636	8458.1722	-3076.8520	30479.3279	0.3	2244.0701	2248.5659	-280.0583	-290.9822	329.0036	325.2141
Methyl Laurate	Methanol	101.3	1903.9610	1886.9007	-939.5656	6988.0740	0.3	-47.4497	-44.8717	260.2529	256.1479	54.4589	57.5334
Methyl Laurate	Ethanol	101.3	1660.0136	-198.9931	-1316.0741	7965.2513	0.3	8.8791	-41.6727	69.2870	115.6599	-4.9094	-89.7449
Methyl Laurate	Methyl Myristate	13.33	240.4782	-225.8835	5509.1993	-3747.3643	0.3	5181.3534	8188.7093	-	-	-	-
		6.6	2370.8331	-1790.0731	19894.9696	-2783.3508	0.3	5149.9794	8130.3104	-	-	-	-
		5.3	1426.1790	-1199.9965	4298.4132	-3216.9545	0.2	5113.9813	8247.5154	-	-	-	-
		4	-1360.9834	1613.1481	-3822.3186	5093.7199	0.3	4940.1199	7967.0967	-	-	-	-
Methyl Laurate	Lauric acid	0.533	2984.7922	-2009.6239	7010.1581	-3873.4973	0.3	-26.2345	149.7382	597.4478	-218.9839	705.6705	3785.6908
Methyl Myristate	Methanol	101.3	3932.9711	-57.9391	1770.8382	1770.2218	0.3	257.0185	254.7454	-	-	-	-
Methyl Myristate	Ethanol	101.3	-519.3354	4994.9654	1672.1490	1672.1637	0.3	-179.2730	-192.2858	542.5894	551.8788	275.1600	287.9658
Methyl myristate	Methyl pamitate	3.9997	45.5099	40.1149	-1600.7794	14616.7305	0.3	6631.2728	4800.5185	-	-	-	-
Methyl myristate	Methyl pamitate	5.33	1853.4863	-1481.5938	-4661.3027	3889.7643	0.3	6103.7831	6124.6777	-			
Methyl palmitate	Methyl stearate	0.533	3492.1874	-2253.2184	10079.5863	-4343.4433	0.3	4604.2393	6664.5012	-	-	-	-
Methyl palmitate	Methyl linoleate	4	-2495.2162	3989.3436	-4250.6943	11589.0549	0.3	-4897.6163	2440.5952	6781.6863	3620.7318	-691.4369	-4602.0844
Methyl Oleate	Methanol	90	-151.4517	4281.9191	8806.9228	-728.1267	0.3	-	-	-	-	-	-

Table 1: Thermodynamic model parameters for VLE data and systems involving lipids. **(Continuation)**

Methyl Oleate	Methanol	70	-189.2620	4401.2316	8867.0692	-868.3735	0.3	-	-	-	-	-	-
Methyl Oleate	Methanol	50	-209.6745	4464.4714	8961.1581	-994.1093	0.3	-	-	-	-	-	-
Methyl Oleate	Methanol	101.3	-93.4075	4117.3091	10013.5727	-1602.7057	0.3	-	-	-	-	-	-
Methyl Oleate	Methanol	30	140.0530	3515.3506	11574.4073	-2352.4692	0.3	-	-	-	-	-	-
Methyl Oleate	Methanol	101.3	-130.9401	4226.2752	10407.0254	-1798.5800	0.3	238.0166	2075.7543	485.2091	40.9412	505.5544	193.7500
Methyl Oleate	Ethanol	101.3	439.2769	865.7709	1806.2782	-2015.5586	0.3	-23.5311	-15.4812	143.5594	134.5271	18.4920	18.6553
Ethyl palmitate	Ethyl stearate	5.3329	2.0501	2.0898	-2907.6639	2574.6124	0.3	5646.0081	9460.9517	-	-	-	-
Ethyl Palmitate	Ethyl oleate	5.3329	-2631.6178	4160.9488	-4942.9566	13156.2028	0.3	4246.4340	38687.1406	9988.4738	6365.0275	107.8410	26344.9696
Ethyl Palmitate	Ethyl oleate		-2040.4244	2753.8341	-4818.9720	8723.8389	0.3	128.2893	144.1771	9671.8117	9998.0630	-481.0546	-124.6379
Ethyl linoleate	Ethyl Palmitate	9.3326	-368.8759	352.0901	-1762.3157	1591.3796	0.3	1.6109	1.6057	1.2210	-316.9307	34.9401	1.6364
Glycerol	Water	101	-763.0625	238.1135	-522.3200	-2226.7470	0.3	9193.3678	-3589.3976	245.8128	-3087.9000	245.7509	-244.2756
Glycerol	Water	101.325	87090.4287	233778.4192	-1436.4817	-1439.3325	0.3	11183.6757	6743.7640	877.9217	-335.0086	814.4209	-53.5057
Glycerol	Water	95.3	-1374.6780	1227.5366	-3400.3001	364.2217	0.3	49.8230	-15.4387	34.3509	41.6276	116.1005	-169.5951
		63.84	-2765.2027	2120.2122	-5049.9832	667.1793	0.3	126.8151	98.9449	25.0380	7.6785	8.0212	-187.5292
		54.72	-1314.3089	977.1529	-3556.8832	1391.3828	0.3	3744.1184	7763.9990	329.1410	781.4933	302.8994	-274.7591
		41.54	-291.6625	-293.8185	-1306.7887	-1312.1305	0.3	-18.1490	-176.5831	226.4295	369.9235	292.2456	-398.8097
		29.38	-448.0202	317.1587	-814.6999	-815.8348	0.3	98.1261	-85.7234	92.8794	236.0244	106.7543	-175.8585
		14.19	-1502.4059	1162.7773	-1324.7462	-1334.9632	0.3	5519.6391	-2219.2209	304.1686	-1783.8615	303.8544	-273.0852

Table 1: Thermodynamic model parameters for VLE data and systems involving lipids. **(Continuation)**

Glycerol	Ethanol	101.3	830.7324	824.6056	7240.2222	-1819.1493	0.3	-	-	5349.8756	9191.5154	-	-
		66.7	1074.1056	1073.8617	3596.9131	3578.8544	0.3	4672.4790	4655.2745	-	-	-	-
		60	1071.9648	1064.4734	3576.8103	3575.8534	0.3	4707.0161	4379.6629	-	-	-	-
		53.3	1059.4421	1059.2631	3548.5687	3547.6085	0.3	4672.8818	4655.3373	-	-	-	-
		46.7	1027.9765	1027.6186	3427.1683	3426.1125	0.3	4370.6385	4352.2163	-	-	-	-
Ethanol	Glycerol	40	780.3393	774.7638	1185.4704	6440.1406	0.3	4776.6743	4423.0018	-	-	-	-
		33.3	765.8262	760.3825	1152.4383	6282.3822	0.3	4624.7111	4272.6240	-	-	-	-
		20	743.1218	742.5153	1101.9328	6178.5215	0.3	3754.1038	3482.4898	-	-	-	-
		13.3	712.3277	707.3049	1654.9173	3612.7696	0.3	4279.8663	9274.6679	-	-	-	-
		6.7	664.5092	659.7772	891.4886	5220.1711	0.3	4140.8004	8826.5247	-	-	-	-
		101.3	5.5190	2.9844	-1973.5111	5619.1862	0.3	-85.3575	-85.3575	4.6889	4.6871	93.3445	93.3436
		90	4.5654	3.8305	740.6547	751.1805	0.3	-86.7588	-86.7590	3.4072	3.4055	92.3383	92.3377
Glycerol	Methanol	70	6.0606	2.6840	467.4657	474.2602	0.3	-88.3477	-88.3476	4.3196	4.3177	95.6339	95.6330
		50	6.2489	2.5163	-1653.5029	5270.6156	0.3	-88.8295	-88.8295	4.0889	4.0869	95.6232	95.6222
		30	742.3683	740.6446	9591.3024	9598.1324	0.3	-90.7991	-90.7991	3.9523	3.9501	97.1792	97.1774

Table 1: Thermodynamic model parameters for VLE data and systems involving lipids**(Continuation)**

Glycerol	Methanol	101	697.3159	697.2463	-2153.1561	4987.3577	0.3	-81.6143	-81.7697	5.2820	5.2661	93.1339	92.8376
Glycerol	Methanol	32.02	3273.2824	-994.7604	874.0900	872.0854	0.3	-65.5698	-65.7481	23.8159	23.8167	113.5904	113.3023
		45.3	3168.3481	-1055.4955	677.6802	675.8448	0.3	3.6697	40.7772	241.9169	2.8410	461.1137	-162.7726
Methanol	Glycerol	66.7	1666.7790	1654.5298	2054.7732	2042.0353	0.3	-171.2876	-172.3767	14.6137	-4.4003	243.5153	218.4271

Table 2: Thermodynamic model parameters for SLE data and lipids systems

BINARY MIXTURE		NRTL MODEL			UNIQUAC MODEL		UNIFAC MODEL						FST		
LIPID	Second compound	g12-g22 (J/mol)	g21-g11 (J/mol)	a_{12}	u12-u22 (J/mol)	u21-u11 (J/mol)	a12	a21	a13	a31	a23	a32	c	a	b
Lauric Acid	Myristic acid	-613.0953	-612.7214	0.3	-70.7449	-70.7216	-9991.9284	-7477.1936	-	-	-	-	-6.9561	0.0002	-7.5488
		131.9358	131.7920	0.3	15.5409	15.5292	15145.2432	2951.4043	-	-	-	-	-1717.7137	5.6052	-74.3879
Lauric Acid	Myristic acid	-8777.9216	-8773.6336	0.3	-1425.4840	-1424.3219	-9629.7563	-9998.7970	-	-	-	-	-0.0001	5.6290	-2091.2247
		-	-	-	-3145.5656	-3140.4453	30941.6623	-9987.2021	-	-	-	-			
Lauric Acid	Myristic acid	-556.0927	-556.0381	0.3	-63.8771	-63.8532	-69452.7153	-7195.1990	-	-	-	-	-0.0001	3.4189	-1108.6192
		-399.8134	-390.6622	0.3	-43.3902	-42.2309	-6815.7424	-7412.7347	-	-	-	-	-0.0001	1.3476	-425.1176
Lauric Acid	Myristic acid	-69.9881	-69.3213	0.3	-6.5325	-6.4925	-4984.1417	-761.8436	-	-	-	-	-0.0001	2.5140	-809.2620
		-276.2616	-271.0576	0.3	-29.0331	-28.3896	-5823.3950	-6915.8973	-	-	-	-	-0.0001	0.0001	-1.9179
Lauric Acid	Palmitic acid	-828.6099	-818.7250	0.3	-84.2147	-84.2042	-6064.9679	-8480.1640	-	-	-	-	-0.0001	5.0128	-1668.9337
		-4210.9079	-4205.0926	0.3	-503.2420	-503.1069	-7388.2797	-7274.7968	-	-	-	-	-1.7367	4.8467	-1535.3208
Lauric Acid	Stearic Acid	-166.7324	-166.7208	0.3	-8.4207	-8.4141	-3438.8416	-234.1966	-	-	-	-	-0.0001	2.5445	-853.0006
		-3621.9654	-3640.9199	0.3	-345.1865	-333.0319	-4098.7341	-9998.4114	-	-	-	-	-0.0001	0.4313	-141.1822
Lauric Acid	Stearic acid	-195.6560	-195.6463	0.3	-11.6250	-11.6146	-4221.2849	-327.6422	-	-	-	-	-0.0001	2.3406	-787.2268
		-3621.9634	-3640.9202	0.3	-345.1800	-333.0367	-4108.7475	-9998.4035	-	-	-	-	-0.0001	1.5431	-492.5591

Table 2: Thermodynamic model parameters for SLE data and lipids systems **(Continuation)**

Lauric Acid	Stearic acid	-89.3432	-89.1473	0.3	0.1487	0.1486	-143.9616	246.0132	-	-	-	-	-0.0001	2.6787	-892.0413
		92.1142	92.0918	0.3	14.8372	14.8195	7230.1720	4849.7499	-	-	-	-	-0.0035	7.0225	-2217.4939
Myristic acid	Palmitic acid	-489.8962	-489.7725	0.3	-49.3785	-49.3474	-9985.7656	-7531.5483	-	-	-	-	-0.0001	4.1575	-1382.9856
		2189.1262	2186.1329	0.3	198.7722	198.6742	44011.0233	2426.1107	-	-	-	-	-0.0001	1.3327	-579.1896
Myristic acid	Palmitic acid	-532.7177	-532.5994	0.3	-53.9114	-53.8777	-9980.4749	-8045.3106	-	-	-	-	-0.0001	3.0151	-1005.5578
		-552.7972	-539.9497	0.3	-54.8809	-53.4671	-9997.1209	-7516.2351	-	-	-	-	-0.0001	1.4152	-462.9677
Myristic acid	Stearic acid	-260.8886	-258.6466	0.3	-21.1645	-20.9115	-8059.1908	-961.2092	-	-	-	-	-0.0001	2.1154	-718.8572
		-2570.7237	-2568.1904	0.3	-243.5545	-243.3069	-9322.7185	-7741.6156	-	-	-	-	-0.0001	4.6783	-1530.9374
Myristic acid	Stearic acid	-204.3974	-202.8936	0.3	-16.1136	-15.9606	-7985.5697	-806.2244	-	-	-	-	-0.0001	4.1028	-1382.0092
		-1813.9268	-1813.1661	0.3	-161.9857	-161.7756	4964.2247	-7349.0534	-	-	-	-	-0.0001	4.6783	-1530.9374
Palmitic acid	Stearic acid	119.7017	118.0776	0.3	11.6214	11.6180	18801.5804	2673.1895	-	-	-	-	-0.0001	2.7493	-925.9389
		-1255.7273	-1255.5124	0.3	-118.1233	-118.0308	-9800.0000	-6614.0764	-	-	-	-	-0.0001	3.7532	-1412.7826
Palmitic acid	Linoleic acid	365.1044	364.9216	0.3	36.1420	36.1419	-	-	-	-	-	-	-333.5370	4.1322	-0.0001
Oleic acid	Stearic acid	-1484.5281	-1484.5785	0.3	-86.3668	-88.5699	473.4943	225.2024	-5914.9998	-1022.1851	901.6190	227.8225			
Stearic acid	Acetone	799.1327	795.4503	0.2	1059.9170	1038.9970	-	-	-	-	-	-	-333.1791	1.2854	-139.4613
Linoleic acid	Oleic acid	-611.9181	-606.0935	0.3	-60.0904	-60.0857	6402.8969	206.7686	-1425.9922	-297.1466	1082.3162	-2240.0680	-0.0001	2.4293	-702.2132
		3467.0549	3461.3297	0.3	294.3772	294.2084	-	-	-	-	-	-	-409.0825	1.5554	-0.0001

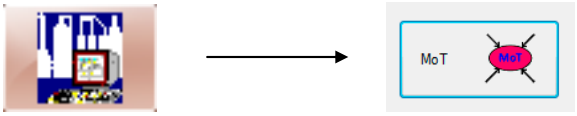
Table 2: Thermodynamic model parameters for SLE data and lipids systems **(Continuation)**

Oleic acid	Palmitic acid	-86.1545	-86.1225	0.3	-8.1931	-8.1836	-	-	-	-	-	-	-8.6804	2.4018	-771.9300
POP	PPP	-7486.7828	-7487.6076	0.2	-386.1691	-387.6022	-241.3291	-189.8881	3878.1487	476.8932	7.7101	109.1421	-0.0001	9.9649	-4111.7186
Triolein	Tripalmitin	850.9836	849.7403	0.3	27.8568	27.5869	2735.8497	374.7245	-5656.7767	-1348.3105	6904.3362	1049.7332	-140.3732	0.4657	-0.0001
Triolein	Tripalmitin	813.0641	812.9977	0.3	26.5415	26.5396	-	-	-	-	-	-	-177.7303	1.5105	-323.9379
Oleic acid	Tripalmitin	1284.0005	1289.1537	0.3	134.0584	134.1003	-	-	-	-	-	-	-292.9416	0.8765	-0.0001
Oleic acid	Tripalmitin	1339.7730	1343.7234	0.3	132.6522	132.7393	-	-	-	-	-	-	-281.4936	0.8712	-0.0001
Oleic acid	Tripalmitin	1990.2957	1990.3031	0.3	152.9075	153.0011	-	-	-	-	-	-	-263.7009	0.9451	-0.0001
Linoleic	Tripalmitin	1377.6076	1376.8645	0.3	120.7949	121.4899	-	-	-	-	-	-	-249.3836	0.8017	-0.0001
Triolein	Palmitic acid	-1373.5466	-1379.0499	0.3	41.2300	41.2298	-	-	-	-	-	-	-32.1596	0.0307	-0.0001
Triolein	Palmitic acid	573.9574	575.5984	0.3	77.8647	77.8305	-	-	-	-	-	-	-247.2192	4.6910	-1295.1872
Triolein	Palmitic acid	-238.6995	-238.8228	0.3	-108.3776	-108.3650	-	-	-	-	-	-	-14.1256	0.0001	-12.8940
M-Laurate	M-Stearate	-1171.4004	-1168.8197	0.3	-120.0157	-119.8633	-9665.6157	-7055.0156	-	-	-	-	-239.0270	7.8753	-2276.8822
M-Myristate	M-Palmitate	131.6403	129.5560	0.3	13.3343	13.3301	18518.9189	2480.9822	-	-	-	-	-0.0001	0.9932	-283.2845
M-Palmitate	M-Stearate	-1488.3191	-1480.8027	0.3	263.0876	262.4664	30090.9853	3118.7221	-	-	-	-	-420.1534	1.7172	-41.5235
M-Palmitate	M-Stearate	-21.3130	-21.2901	0.3	-1.3218	-1.3204	-2184.8889	-342.6027	-	-	-	-	-340.5482	12.6261	-3582.1825
		-1413.2722	-1377.3369	0.3	-128.2719	-124.0515	-6209.6176	-6423.1389	-	-	-	-	-361.3157	9.1376	-2402.0878

Table 2: Thermodynamic model parameters for SLE data and lipids systems **(Continuation)**

M-Myristate	M-Stearate	65.7460	65.2960	0.3	8.9746	8.9738	14281.5280	3022.6493	-	-	-	-	-54.0750	5.0189	-1484.7613
		-5175.9990	-5168.2845	0.3	-642.0962	-641.8941	-6014.0615	-6434.9718	-	-	-	-	-0.0001	8.4599	-2473.1300
M-Oleate	M-Stearate	-1334.7707	-1331.9248	0.3	-128.1132	-128.1104	604.4677	34.4265	-2692.9260	-563.9128	22.9594	-45.9417	-125.4105	2.9056	-873.9246
M-Linoleate	M-Stearate	-1454.3439	-1451.2288	0.3	-147.9497	-143.0302	-980.6617	-2.6962	-1697.7048	-547.8165	231.5379	1168.7064	-181.4009	6.4577	-1902.8728
E-Laurate	E-Palmitate	3047.5355	3030.8339	0.3	257.0376	255.5247	24987.2788	2692.9373	-	-	-	-	-28.2542	0.5155	-0.0001
E-Myristate	E-Palmitate	3620.5804	3590.8287	0.3	278.2871	275.2586	38296.7418	2351.7804	-	-	-	-	-55.6492	1.4781	-273.8637
		20984.8049	20960.5192	0.3	-2428.1662	-2425.8393	76720.3690	2462.8512	-	-	-	-	-207.0412	0.7445	-0.0001
E-Myristate	E-Stearate	1473.9864	1467.5552	0.3	124.9130	124.5610	21533.5585	2607.2232	-	-	-	-	-170.3171	0.6838	-0.0001
E-Palmitate	E-Oleate	2564.3755	2560.3922	0.3	197.9516	197.6382	-9551.3120	-18437.9472	7927.9052	181.7633	1653.1732	-567.4938	-35.7163	0.5919	-0.0001
E-Laurate	E-Stearate	1932.9109	1927.5665	0.3	175.0943	174.8584	17814.4469	2836.2155	-	-	-	-	-316.4236	1.6500	-149.5944
E-Linoleate	E-Stearate	1859.7883	1855.4164	0.3	144.6188	144.2087	-5028.2959	237.6621	918.6948	130.6451	272.6865	431.2251	-304.1865	1.6385	-161.5578
E-Palmitate	E-Linoleate	604.4341	603.5598	0.3	209.8639	209.8469	506.3434	329.4188	86.2226	-35.3696	332.0292	110.4300	-	-	-

Appendix 3



VLE – NRTL Model (Temperature calculation)

#NRTL model for liquid phase

Parameter estimation for NRTL model for binary mixtures and isobaric
systems and Bubble T calculation
NRTL model + Ideal Vapour Phase

CAPEC 2012 Larissa P. Cunico

#**

#Variable and parameters description

# P	Pressure [kPa]
# T	Temperature [K]
# X	Mole fraction of the liquid phase
# Y	Mole fraction of the vapour phase
# R	Universal gas constant
# Gamma	Activity coefficient

par1=g12-g22 , par2=g21-g11 , alpha_1_2 Parameters estimated

#**

For the liquid phase - NRTL model equations:

#Calculate Mol fraction 2
X2[r] = 1 - X1[r]

```
Y2[r] = 1 - Y1[r]


# Model equations:

# Calculate interaction terms Tau and G
# par1=g12-g22
# par2=g21-g11
Tau_1_2[r]= par1/(R*T[r])
Tau_2_1[r]= par2/(R*T[r])

G_1_2[r] = exp(-alpha_1_2*Tau_1_2[r])
G_2_1[r] = exp(-alpha_1_2*Tau_2_1[r])

#Calculate Ln(Gamma)for liquid phase
LnGammal_1[r]= X2[r]^2*Tau_2_1[r]*(G_2_1[r]/(X1[r]+X2[r]*G_2_1[r]))^2 +
X2[r]^2*Tau_1_2[r]*G_1_2[r]/(X2[r]+X1[r]*G_1_2[r])^2
LnGammal_2[r]= X1[r]^2*Tau_1_2[r]*(G_1_2[r]/(X2[r]+X1[r]*G_1_2[r]))^2 +
X1[r]^2*Tau_2_1[r]*G_2_1[r]/(X1[r]+X2[r]*G_2_1[r])^2


Gamma1[r] = exp(LnGammal_1[r])
Gamma2[r] = exp(LnGammal_2[r])


#*********************************************************************

# Saturation pressure calculation (equation from CAPEC_database)
P_sat1[r]=(exp(A11+(B11/T[r])+(C11*ln(T[r]))+(D11*T[r]^E11)))/1000
P_sat2[r]=(exp(A22+(B22/T[r])+(C22*ln(T[r]))+(D22*T[r]^E22)))/1000

# Saturation pressure calculation (Antoine equation)
#P_sat1[r]=(10^(AA1-(BB1/(CC1+T[r]))))*0.001
#P_sat2[r]=(10^(AA2-(BB2/(CC2+T[r]))))*0.001

#Calculation of y (vapour molar fraction)
Ycalc_1[r] = (Gamma1[r]*(P_sat1[r]*X1[r]))/P
Ycalc_2[r] = (Gamma2[r]*(P_sat2[r]*X2[r]))/P

0=1-Ycalc_1[r]-Ycalc_2[r]
```

```
# Objective Function – Least Square
Res1[r] =(T[r] - Texp[r])

Fobj = (sum_{r}((Res1[r])^2)/N))

#Maximum likelihood function for a normal distribution
  error[r] = abs(Texp[r] - T[r])^2
  SSUM     = sum_r(error[r])
  res1[r] = abs(T[r]-Texp[r])
  RSUM     = sum_r((res1[r])^2)

 Obj_lnf  = -(-0.5*NN*ln(2*PI) - NN*ln(SIGMA) - SSUM/(2*SIGMA^2) )
```

VLE – UNIQUAC Model (Temperature calculation)

```
# UNIQUAC model for the liquid phase

# Parameter estimation for UNIQUAC model for binary mixtures and
# isobaric systems and Bubble T calculation
# UNIQUAC model + Ideal vapour phase

# Capec 2012 Larissa P. Cunico

#**********************************************************************

#Variable and parameters description

# P                     Pressure [kPa]
# T                     Temperature [K]
# X                     Mole fraction of the liquid phase
# Y                     Mole fraction of the vapour phase

# R                     Universal gas constant
# Gamma                     Activity coefficient

# u12_u22 , u21_u11         Parameters estimated for UNIQUAC model
# r, q                          Parameters listed for UNIQUAC model


#**********************************************************************


# For the liquid phase - UNIQUAC model equations:

#Calculate Mol fraction 2
 X2[r] = 1 - X1[r]
 Y2[r] = 1 - Y1[r]

#For the calculation of volume parameter (r) and surface area
# parameter (q)
r1 = sum_k(v1[k]*R[k])
r2 = sum_k(v2[k]*R[k])
q1 = sum_k(v1[k]*Q[k])
q2 = sum_k(v2[k]*Q[k])
```

```
#Calculation of gamma of liquid phase
 Ph1[r] = (r1*X1[r])/(r1*X1[r]+r2*X2[r])
 Ph2[r] = (r2*X2[r])/(r1*X1[r]+r2*X2[r])

 Theta1[r] = (q1*X1[r])/(q1*X1[r]+q2*X2[r])
 Theta2[r] = (q2*X2[r])/(q1*X1[r]+q2*X2[r])

 l1 = 5*(r1-q1)-(r1-1)
 l2 = 5*(r2-q2)-(r2-1)

 Tau12[r] = exp(-u12_u22/(R*T[r]))
 Tau21[r] = exp(-u21_u11/(R*T[r]))


 A1[r]= q1*ln(Theta1[r]+Theta2[r]*Tau21[r])
 A2[r]= q2*ln(Theta2[r]+Theta1[r]*Tau12[r])

 C1[r]=(Tau21[r]/(Theta1[r]+Theta2[r]*Tau21[r]))-(Tau12[r]/(Theta2[r]+Theta1[r]*Tau12[r]))
 C2[r]=(Tau12[r]/(Theta2[r]+Theta1[r]*Tau12[r]))-(Tau21[r]/(Theta1[r]+Theta2[r]*Tau21[r]))


 lnGamma1[r] = ln(Ph1[r]/X1[r]) + 5*q1*ln(Theta1[r]/Ph1[r])+Ph2[r]*(l1-(l2*(r1/r2)))- A1[r] +
Theta2[r]*q1*C1[r]
 lnGamma2[r] = ln(Ph2[r]/X2[r]) + 5*q2*ln(Theta2[r]/Ph2[r])+Ph1[r]*(l2-(l1*(r2/r1)))- A2[r] +
Theta1[r]*q2*C2[r]

 Gamma1[r] = exp(lnGamma1[r])
 Gamma2[r] = exp(lnGamma2[r])


#*********************************************************************

# Saturation pressure calculation (equation from CAPEC_database)
P_sat1[r]=(exp(A11+(B11/T[r])+(C11*ln(T[r]))+(D11*T[r]^E11)))/1000
P_sat2[r]=(exp(A22+(B22/T[r])+(C22*ln(T[r]))+(D22*T[r]^E22)))/1000

# Saturation pressure calculation (Antoine equation)
#P_sat1[r]=(10^(AA1-(BB1/(CC1+T[r]))))*0.001
#P_sat2[r]=(10^(AA2-(BB2/(CC2+T[r]))))*0.001
```

```
#Calculation of y (vapour molar fraction)
Ycalc_1[r] = (Gamma1[r]*(P_sat1[r]*X1[r]))/P
Ycalc_2[r] = (Gamma2[r]*(P_sat2[r]*X2[r]))/P

0=1-Ycalc_1[r]-Ycalc_2[r]

# Objective Function – Least Square
Res1[r] =(T[r] - Texp[r])

Fobj = (sum_{r}((Res1[r])^2)/N))

#Maximum likelihood function for a normal distribution
  error[r] = abs(Texp[r] - T[r])^2
  SSUM     = sum_r(error[r])
  res1[r] = abs(T[r]-Texp[r])
  RSUM     = sum_r((res1[r])^2)

 Obj_lnf  = -(-0.5*NN*ln(2*PI) - NN*ln(SIGMA) - SSUM/(2*SIGMA^2) )
```

VLE – UNIFAC Model (Temperature calculation)

```
# UNIFAC-VLE model for the liquid phase

# Parameter estimation for UNIFAC model for binary mixtures and
# isobaric systems and Bubble T calculation
# UNIFAC model
# Ideal vapour phase

#*Mauricio Sales-Cruz
#*CAPEC, DTU, DK
#*15.02.05

#+ modifications
# Capec 2012 Larissa P. Cunico

#*********************************************************************



#Variable and parameters description

# P                     Pressure [kPa]
# T                     Temperature [K]
# X                     Mole fraction of the liquid phase
# Y                     Mole fraction of the vapour phase

# R                     Universal gas constant
# Gamma                 Activity coefficient
# GammaC                Activity coefficient combinatorial
# GammaR                Activity coefficient residual

#v1[k]                      Number of groups of kind k

# r, q                      Pure component volume and are parameters
# Rk, Qk                        Group volume and area parameters
# -a1[n]                    Group binary interaction parameters


#*********************************************************************
# ATTETION the number of the first index of Tao1[0][k][r] (in this case 0) should be changed
```

```
#Calculate Mol fraction 2

 X2[r] = 1 - X1[r]

#Model equations:

  r1 = sum_k(v1[k]*R[k])
  r2 = sum_k(v2[k]*R[k])
  q1 = sum_k(v1[k]*Q[k])
  q2 = sum_k(v2[k]*Q[k])

  G1[k]  = v1[k]*Q[k]
  G2[k]  = v2[k]*Q[k]

  Theta[k][r] = (G1[k]*X1[r])+(G2[k]*X2[r])

# The interaction parameters should not vary in the subgroups
# Set of condition for binary interaction parameters of CH3 (1) and CH2 (2)
  a[0][2] = a[1][2]
  a[2][0] = a[2][1]

  Tao[0][k][r] = exp((-a[0][k])/(T[r]))
  Tao[1][k][r] = exp((-a[1][k])/(T[r]))
  Tao[2][k][r] = exp((-a[2][k])/(T[r]))

  s1[k][r]  = (G1[0]*Tao[0][k][r])+(G1[1]*Tao[1][k][r])+(G1[2]*Tao[2][k][r])
  s2[k][r]  = (G2[0]*Tao[0][k][r])+(G2[1]*Tao[1][k][r])+(G2[2]*Tao[2][k][r])

  eta[k][r]   = (s1[k][r]*X1[r])+(s2[k][r]*X2[r])

  J1[r] = r1/(r1*X1[r]+r2*X2[r])
  J2[r] = r2/(r1*X1[r]+r2*X2[r])
  L1[r] = q1/(q1*X1[r]+q2*X2[r])
  L2[r] = q2/(q1*X1[r]+q2*X2[r])

  lnGammaC1[r] = 1 - J1[r] + ln(J1[r]) - 5*q1*(1 - J1[r]/L1[r] + ln(J1[r]/L1[r]))
  lnGammaC2[r] = 1 - J2[r] + ln(J2[r]) - 5*q2*(1 - J2[r]/L2[r] + ln(J2[r]/L2[r]))

  I1[k][r] = ((Theta[k][r]*s1[k][r]/eta[k][r] - G1[k]*ln(s1[k][r]/eta[k][r])))
  I2[k][r] = ((Theta[k][r]*s2[k][r]/eta[k][r] - G2[k]*ln(s2[k][r]/eta[k][r])))
```

```
  lnGammaR1[r] = q1*(1 - ln(L1[r])) - (I1[0][r]+ I1[1][r]+I1[2][r])
  lnGammaR2[r] = q2*(1 - ln(L2[r])) - (I2[0][r]+ I2[1][r]+I2[2][r])

  LnGammal_1[r]  = lnGammaC1[r] + lnGammaR1[r]
  LnGammal_2[r]  = lnGammaC2[r] + lnGammaR2[r]

  Gamma1[r] = exp(LnGammal_1[r])
  Gamma2[r] = exp(LnGammal_2[r])


#*********************************************************************

# Saturation pressure calculation (equation from CAPEC_database)
P_sat1[r]=(exp(A11+(B11/T[r])+(C11*ln(T[r]))+(D11*T[r]^E11)))/1000
P_sat2[r]=(exp(A22+(B22/T[r])+(C22*ln(T[r]))+(D22*T[r]^E22)))/1000

# Saturation pressure calculation (Antoine equation)
#P_sat1[r]=(10^(AA1-(BB1/(CC1+T[r]))))*0.001
#P_sat2[r]=(10^(AA2-(BB2/(CC2+T[r]))))*0.001

#Calculation of y (vapour molar fraction)
Ycalc_1[r] = (Gamma1[r]*(P_sat1[r]*X1[r]))/P
Ycalc_2[r] = (Gamma2[r]*(P_sat2[r]*X2[r]))/P

0=1-Ycalc_1[r]-Ycalc_2[r]

# Objective Function – Least Square
Res1[r] =(T[r] - Texp[r])

Fobj = (sum_{r}((Res1[r])^2)/N))

#Maximum likelihood function for a normal distribution
  error[r] = abs(Texp[r] - T[r])^2
  SSUM     = sum_r(error[r])
  res1[r] = abs(T[r]-Texp[r])
  RSUM     = sum_r((res1[r])^2)

 Obj_lnf  = -(-0.5*NN*ln(2*PI) - NN*ln(SIGMA) - SSUM/(2*SIGMA^2) )
```

VLE – NRTL Model (Molar fraction calculation)

```
#NRTL model for liquid phase

# Parameter estimation for NRTL model for binary mixtures and isobaric
# systems and Bubble T calculation
# NRTL model + Ideal Vapour Phase

# CAPEC 2012 Larissa P. Cunico

#*********************************************************************

#Variable and parameters description

# P                                 Pressure [kPa]
# T                                 Temperature [K]
# X                                 Mole fraction of the liquid phase
# Y                                 Mole fraction of the vapour phase

# R                                 Universal gas constant
# Gamma                                 Activity coefficient

# par1=g12-g22 ,  par2=g21-g11 , alpha_1_2          Parameters estimated

#*********************************************************************


# For the liquid phase - NRTL model equations:

#Calculate Mol fraction 2
 X2[r] = 1 - X1[r]
 Y2[r] = 1 - Y1[r]


# Model equations:

# Calculate interaction terms Tau and G
# par1=g12-g22
# par2=g21-g11
Tau_1_2[r]= par1/(R*T[r])
```

```
Tau_2_1[r]= par2/(R*T[r])

G_1_2[r] = exp(-alpha_1_2*Tau_1_2[r])
G_2_1[r] = exp(-alpha_1_2*Tau_2_1[r])

#Calculate Ln(Gamma)for liquid phase
LnGammal_1[r]= X2[r]^2*Tau_2_1[r]*(G_2_1[r]/(X1[r]+X2[r]*G_2_1[r]))^2 +
X2[r]^2*Tau_1_2[r]*G_1_2[r]/(X2[r]+X1[r]*G_1_2[r])^2
LnGammal_2[r]= X1[r]^2*Tau_1_2[r]*(G_1_2[r]/(X2[r]+X1[r]*G_1_2[r]))^2 +
X1[r]^2*Tau_2_1[r]*G_2_1[r]/(X1[r]+X2[r]*G_2_1[r])^2


Gamma1[r] = exp(LnGammal_1[r])
Gamma2[r] = exp(LnGammal_2[r])


#*********************************************************************

# Saturation pressure calculation (equation from CAPEC_database)
P_sat1[r]=(exp(A11+(B11/T[r])+(C11*ln(T[r]))+(D11*T[r]^E11)))/1000
P_sat2[r]=(exp(A22+(B22/T[r])+(C22*ln(T[r]))+(D22*T[r]^E22)))/1000

# Saturation pressure calculation (Antoine equation)
#P_sat1[r]=(10^(AA1-(BB1/(CC1+T[r]))))*0.001
#P_sat2[r]=(10^(AA2-(BB2/(CC2+T[r]))))*0.001

#Calculation of y (vapour molar fraction)
Ycalc_1[r] = (Gamma1[r]*(P_sat1[r]*X1[r]))/P
Ycalc_2[r] = (Gamma2[r]*(P_sat2[r]*X2[r]))/P

0=1-Ycalc_1[r]-Ycalc_2[r]

# Objective Function – Least Square
Res1[r] =(X1[r] - X1exp[r])

Fobj = (sum_{r}((Res1[r])^2)/N))

#Maximum likelihood function for a normal distribution

  error[r] = (X1exp[r] - X1[r])^2
```

```
SSUM      = sum_r(error[r])
res1[r] = X1[r]-X1exp[r]
RSUM      = sum_r((res1[r])^2)

Obj_lnf  = -(-0.5*NN*ln(2*PI) - NN*ln(SIGMA) - SSUM/(2*SIGMA^2) )
```

VLE – UNIQUAC Model (Molar fraction calculation)

```
# UNIQUAC model for the liquid phase

# Parameter estimation for UNIQUAC model for binary mixtures and
# isobaric systems and Bubble T calculation
# UNIQUAC model + Ideal vapour phase

# Capec 2012 Larissa P. Cunico

#**********************************************************************

#Variable and parameters description

# P                     Pressure [kPa]
# T                     Temperature [K]
# X                     Mole fraction of the liquid phase
# Y                     Mole fraction of the vapour phase

# R                     Universal gas constant
# Gamma                     Activity coefficient

# u12_u22 , u21_u11         Parameters estimated for UNIQUAC model
# r, q                          Parameters listed for UNIQUAC model


#**********************************************************************


# For the liquid phase - UNIQUAC model equations:

#Calculate Mol fraction 2
 X2[r] = 1 - X1[r]
 Y2[r] = 1 - Y1[r]

#For the calculation of volume parameter (r) and surface area
# parameter (q)
r1 = sum_k(v1[k]*R[k])
r2 = sum_k(v2[k]*R[k])
q1 = sum_k(v1[k]*Q[k])
q2 = sum_k(v2[k]*Q[k])
```

```
#Calculation of gamma of liquid phase
 Ph1[r] = (r1*X1[r])/(r1*X1[r]+r2*X2[r])
 Ph2[r] = (r2*X2[r])/(r1*X1[r]+r2*X2[r])

 Theta1[r] = (q1*X1[r])/(q1*X1[r]+q2*X2[r])
 Theta2[r] = (q2*X2[r])/(q1*X1[r]+q2*X2[r])

 l1 = 5*(r1-q1)-(r1-1)
 l2 = 5*(r2-q2)-(r2-1)

 Tau12[r] = exp(-u12_u22/(R*T[r]))
 Tau21[r] = exp(-u21_u11/(R*T[r]))


 A1[r]= q1*ln(Theta1[r]+Theta2[r]*Tau21[r])
 A2[r]= q2*ln(Theta2[r]+Theta1[r]*Tau12[r])

 C1[r]=(Tau21[r]/(Theta1[r]+Theta2[r]*Tau21[r]))-(Tau12[r]/(Theta2[r]+Theta1[r]*Tau12[r]))
 C2[r]=(Tau12[r]/(Theta2[r]+Theta1[r]*Tau12[r]))-(Tau21[r]/(Theta1[r]+Theta2[r]*Tau21[r]))


 lnGamma1[r] = ln(Ph1[r]/X1[r]) + 5*q1*ln(Theta1[r]/Ph1[r])+Ph2[r]*(l1-(l2*(r1/r2)))- A1[r] +
Theta2[r]*q1*C1[r]
 lnGamma2[r] = ln(Ph2[r]/X2[r]) + 5*q2*ln(Theta2[r]/Ph2[r])+Ph1[r]*(l2-(l1*(r2/r1)))- A2[r] +
Theta1[r]*q2*C2[r]

 Gamma1[r] = exp(lnGamma1[r])
 Gamma2[r] = exp(lnGamma2[r])


#*********************************************************************

# Saturation pressure calculation (equation from CAPEC_database)
P_sat1[r]=(exp(A11+(B11/T[r])+(C11*ln(T[r]))+(D11*T[r]^E11)))/1000
P_sat2[r]=(exp(A22+(B22/T[r])+(C22*ln(T[r]))+(D22*T[r]^E22)))/1000

# Saturation pressure calculation (Antoine equation)
#P_sat1[r]=(10^(AA1-(BB1/(CC1+T[r]))))*0.001
#P_sat2[r]=(10^(AA2-(BB2/(CC2+T[r]))))*0.001
```

```
#Calculation of y (vapour molar fraction)
Ycalc_1[r] = (Gamma1[r]*(P_sat1[r]*X1[r]))/P
Ycalc_2[r] = (Gamma2[r]*(P_sat2[r]*X2[r]))/P

0=1-Ycalc_1[r]-Ycalc_2[r]

# Objective Function – Least Square
Res1[r] =(X1[r] - X1exp[r])

Fobj = (sum_{r}((Res1[r])^2)/N))

#Maximum likelihood function for a normal distribution

 error[r] = (X1exp[r] - X1[r])^2
 SSUM     = sum_r(error[r])
 res1[r] = X1[r]-X1exp[r]
 RSUM     = sum_r((res1[r])^2)

Obj_lnf  = -(-0.5*NN*ln(2*PI) - NN*ln(SIGMA) - SSUM/(2*SIGMA^2) )
```

VLE – UNIFAC Model (Molar fraction calculation)

```
# UNIFAC-VLE model for the liquid phase

# Parameter estimation for UNIFAC model for binary mixtures and
# isobaric systems and Bubble T calculation
# UNIFAC model
# Ideal vapour phase

#*Mauricio Sales-Cruz
#*CAPEC, DTU, DK
#*15.02.05

#+ modifications
# Capec 2012 Larissa P. Cunico

#*********************************************************************



#Variable and parameters description

# P                     Pressure [kPa]
# T                     Temperature [K]
# X                     Mole fraction of the liquid phase
# Y                     Mole fraction of the vapour phase

# R                     Universal gas constant
# Gamma                 Activity coefficient
# GammaC                Activity coefficient combinatorial
# GammaR                Activity coefficient residual

#v1[k]                      Number of groups of kind k

# r, q                      Pure component volume and are parameters
# Rk, Qk                        Group volume and area parameters
# -a1[n]                    Group binary interaction parameters


#*********************************************************************
# ATTETION the number of the first index of Tao1[0][k][r] (in this case 0) should be changed
```

```
#Calculate Mol fraction 2

 X2[r] = 1 - X1[r]

#Model equations:

  r1 = sum_k(v1[k]*R[k])
  r2 = sum_k(v2[k]*R[k])
  q1 = sum_k(v1[k]*Q[k])
  q2 = sum_k(v2[k]*Q[k])

  G1[k]  = v1[k]*Q[k]
  G2[k]  = v2[k]*Q[k]

  Theta[k][r] = (G1[k]*X1[r])+(G2[k]*X2[r])

# The interaction parameters should not vary in the subgroups
# Set of condition for binary interaction parameters of CH3 (1) and CH2 (2)
  a[0][2] = a[1][2]
  a[2][0] = a[2][1]

  Tao[0][k][r] = exp((-a[0][k])/(T[r]))
  Tao[1][k][r] = exp((-a[1][k])/(T[r]))
  Tao[2][k][r] = exp((-a[2][k])/(T[r]))

  s1[k][r]  = (G1[0]*Tao[0][k][r])+(G1[1]*Tao[1][k][r])+(G1[2]*Tao[2][k][r])
  s2[k][r]  = (G2[0]*Tao[0][k][r])+(G2[1]*Tao[1][k][r])+(G2[2]*Tao[2][k][r])

  eta[k][r]   = (s1[k][r]*X1[r])+(s2[k][r]*X2[r])

  J1[r] = r1/(r1*X1[r]+r2*X2[r])
  J2[r] = r2/(r1*X1[r]+r2*X2[r])
  L1[r] = q1/(q1*X1[r]+q2*X2[r])
  L2[r] = q2/(q1*X1[r]+q2*X2[r])

  lnGammaC1[r] = 1 - J1[r] + ln(J1[r]) - 5*q1*(1 - J1[r]/L1[r] + ln(J1[r]/L1[r]))
  lnGammaC2[r] = 1 - J2[r] + ln(J2[r]) - 5*q2*(1 - J2[r]/L2[r] + ln(J2[r]/L2[r]))

  I1[k][r] = ((Theta[k][r]*s1[k][r]/eta[k][r] - G1[k]*ln(s1[k][r]/eta[k][r])))
  I2[k][r] = ((Theta[k][r]*s2[k][r]/eta[k][r] - G2[k]*ln(s2[k][r]/eta[k][r])))
```

```
  lnGammaR1[r] = q1*(1 - ln(L1[r])) - (I1[0][r]+ I1[1][r]+I1[2][r])
  lnGammaR2[r] = q2*(1 - ln(L2[r])) - (I2[0][r]+ I2[1][r]+I2[2][r])

  LnGammal_1[r]  = lnGammaC1[r] + lnGammaR1[r]
  LnGammal_2[r]  = lnGammaC2[r] + lnGammaR2[r]

  Gamma1[r] = exp(LnGammal_1[r])
  Gamma2[r] = exp(LnGammal_2[r])


#*********************************************************************

# Saturation pressure calculation (equation from CAPEC_database)
P_sat1[r]=(exp(A11+(B11/T[r])+(C11*ln(T[r]))+(D11*T[r]^E11)))/1000
P_sat2[r]=(exp(A22+(B22/T[r])+(C22*ln(T[r]))+(D22*T[r]^E22)))/1000

# Saturation pressure calculation (Antoine equation)
#P_sat1[r]=(10^(AA1-(BB1/(CC1+T[r]))))*0.001
#P_sat2[r]=(10^(AA2-(BB2/(CC2+T[r]))))*0.001

#Calculation of y (vapour molar fraction)
Ycalc_1[r] = (Gamma1[r]*(P_sat1[r]*X1[r]))/P
Ycalc_2[r] = (Gamma2[r]*(P_sat2[r]*X2[r]))/P

0=1-Ycalc_1[r]-Ycalc_2[r]

# Objective Function – Least Square
Res1[r] =(X1[r] - X1exp[r])

Fobj = (sum_{r}((Res1[r])^2)/N))

#Maximum likelihood function for a normal distribution

  error[r] = (X1exp[r] - X1[r])^2
  SSUM     = sum_r(error[r])
  res1[r] = X1[r]-X1exp[r]
  RSUM     = sum_r((res1[r])^2)

 Obj_lnf  = -(-0.5*NN*ln(2*PI) - NN*ln(SIGMA) - SSUM/(2*SIGMA^2) )
```

SLE – NRTL Model (Temperature calculation)

```
#NRTL model for liquid phase

# Parameter estimation for NRTL model for binary mixtures and isobaric
# systems

# CAPEC 2012 Larissa P. Cunico


#**********************************************************************

#Variable and parameters description

# P                                 Pressure [kPa]
# T                                 Temperature [K]
# X                                 Mole fraction of the liquid phase
# Y                                 Mole fraction of the vapour phase

# R                                 Universal gas constant
# Gamma                                 Activity coefficient

# par1=g12-g22 ,  par2=g21-g11 , alpha_1_2          Parameters estimated

#**********************************************************************


#Calculate Mol fraction 2
X2[r]= 1 - X1[r]


# Model equations:

# Calculate interaction terms Tau and G
# par1=g12-g22
# par2=g21-g11
Tau_1_2[r]= par1/(R*T[r])
Tau_2_1[r]= par2/(R*T[r])

G_1_2[r] = exp(-alpha_1_2*Tau_1_2[r])
G_2_1[r] = exp(-alpha_1_2*Tau_2_1[r])
```

```
#Calculate Ln(Gamma)for liquid phase
LnGammal_1[r]= X2[r]^2*Tau_2_1[r]*(G_2_1[r]/(X1[r]+X2[r]*G_2_1[r]))^2 +
X2[r]^2*Tau_1_2[r]*G_1_2[r]/(X2[r]+X1[r]*G_1_2[r])^2
LnGammal_2[r]= X1[r]^2*Tau_1_2[r]*(G_1_2[r]/(X2[r]+X1[r]*G_1_2[r]))^2 +
X1[r]^2*Tau_2_1[r]*G_2_1[r]/(X1[r]+X2[r]*G_2_1[r])^2

Gamma1[r] = exp(LnGammal_1[r])
Gamma2[r] = exp(LnGammal_2[r])

#*********************************************************************

0 = ln(X1[r]) + LnGammal_1[r] + (-deltaH1/8.314) *(1/Tm1 - 1/T[r])

#Least Square objective function
res1[r] = T[r]- Texp[r]

Fobj = (sum_r(res1[r])^2))/N


#Maximum likelihood function for a normal distribution
  error[r] = (Texp[r] - T[r])^2
  SSUM     = sum_r(error[r])
  res1[r] = T[r]-Texp[r]
  RSUM     = sum_r((res1[r])^2)

Res_Temp[r] = abs(res1[r]/Texp[r])
Total_Res_Temp = ((sum_r(Res_Temp[r]))*100)/N

Obj_lnf  = -(-0.5*N*ln(2*PI) - N*ln(SIGMA) - SSUM/(2*SIGMA^2) )
```

SLE – UNIQUAC Model (Temperature calculation)

```
# UNIQUAC model for the liquid phase

# Parameter estimation for UNIQUAC model for binary mixtures and
# isobaric systems

# Capec 2012 Larissa P. Cunico

#**********************************************************************

#Variable and parameters description

# P                     Pressure [kPa]
# T                     Temperature [K]
# X                     Mole fraction of the liquid phase
# Y                     Mole fraction of the vapour phase

# R                     Universal gas constant
# Gamma                 Activity coefficient

# u12_u22 , u21_u11     Parameters estimated for UNIQUAC model
# r, q                  Parameters listed for UNIQUAC model


#**********************************************************************


# For the liquid phase - UNIQUAC model equations:

#Calculate Mol fraction 2
 X2[r] = 1 - X1[r]

#For the calculation of volume parameter (r) and surface area parameter (q)
r1 = sum_k(v1[k]*R[k])
r2 = sum_k(v2[k]*R[k])
q1 = sum_k(v1[k]*Q[k])
q2 = sum_k(v2[k]*Q[k])

#Calculation of gamma of liquid phase
 Ph1[r] = (r1*X1[r])/(r1*X1[r]+r2*X2[r])
```

```
Ph2[r] = (r2*X2[r])/(r1*X1[r]+r2*X2[r])

Theta1[r] = (q1*X1[r])/(q1*X1[r]+q2*X2[r])
Theta2[r] = (q2*X2[r])/(q1*X1[r]+q2*X2[r])

l1 = 5*(r1-q1)-(r1-1)
l2 = 5*(r2-q2)-(r2-1)

Tau12[r] = exp(-u12_u22/(R*T[r]))
Tau21[r] = exp(-u21_u11/(R*T[r]))


A1[r]= q1*ln(Theta1[r]+Theta2[r]*Tau21[r])
A2[r]= q2*ln(Theta2[r]+Theta1[r]*Tau12[r])

C1[r]=(Tau21[r]/(Theta1[r]+Theta2[r]*Tau21[r]))-(Tau12[r]/(Theta2[r]+Theta1[r]*Tau12[r]))
C2[r]=(Tau12[r]/(Theta2[r]+Theta1[r]*Tau12[r]))-(Tau21[r]/(Theta1[r]+Theta2[r]*Tau21[r]))


LnGammal_1[r] = ln(Ph1[r]/X1[r]) + 5*q1*ln(Theta1[r]/Ph1[r])+Ph2[r]*(l1-(l2*(r1/r2)))- A1[r] +
Theta2[r]*q1*C1[r]
LnGammal_2[r] = ln(Ph2[r]/X2[r]) + 5*q2*ln(Theta2[r]/Ph2[r])+Ph1[r]*(l2-(l1*(r2/r1)))- A2[r] +
Theta1[r]*q2*C2[r]

Gamma1[r] = exp(LnGammal_1[r])
Gamma2[r] = exp(LnGammal_2[r])

#*********************************************************************

0 = ln(X1[r]) + LnGammal_1[r] + (-deltaH1/8.314) *(1/Tm1 - 1/T[r])

#Least Square objective function
res1[r] = T[r]- Texp[r]

Fobj = (sum_r(res1[r])^2))/N


#Maximum likelihood function for a normal distribution
 error[r] = (Texp[r] - T[r])^2
 SSUM     = sum_r(error[r])
 res1[r] = T[r]-Texp[r]
```

RSUM = sum_r((res1[r])^2)

Res_Temp[r] = abs(res1[r]/Texp[r])

Total_Res_Temp = ((sum_r(Res_Temp[r]))*100)/N

Obj_lnf = -(-0.5*N*ln(2*PI) - N*ln(SIGMA) - SSUM/(2*SIGMA^2))

SLE – original UNIFAC Model (Temperature calculation)

```
# UNIFAC model for the liquid phase

# Parameter estimation for UNIFAC model for binary mixtures and
# isobaric systems

#*Mauricio Sales-Cruz
#*CAPEC, DTU, DK
#*15.02.05

#+ modifications
# Capec 2012 Larissa P. Cunico


#**********************************************************************


#Variable and parameters description

# P                     Pressure [kPa]
# T                     Temperature [K]
# X                     Mole fraction of the liquid phase
# Y                     Mole fraction of the vapour phase

# R                     Universal gas constant
# Gamma                     Activity coefficient
# GammaC                    Activity coefficient combinatorial
# GammaR                    Activity coefficient residual

#v1[k]                          Number of groups of kind k

# r, q                          Pure component volume and are parameters
# Rk, Qk                            Group volume and area parameters
# -a1[n]                        Group binary interaction parameters


#**********************************************************************


# ATTETION the number of the first index of Tao1[0][k][r] (in this case 0) should be changed
```

```
#Calculate Mol fraction 2

 X2[r] = 1 - X1[r]

#Model equations:

  r1 = sum_k(v1[k]*R[k])
  r2 = sum_k(v2[k]*R[k])
  q1 = sum_k(v1[k]*Q[k])
  q2 = sum_k(v2[k]*Q[k])

  G1[k]  = v1[k]*Q[k]
  G2[k]  = v2[k]*Q[k]

  Theta[k][r] = (G1[k]*X1[r])+(G2[k]*X2[r])

# The interaction parameters should not vary in the subgroups
# Set of condition for binary interaction parameters of CH3 (1) and CH2 (2)
  a[0][2] = a[1][2]
  a[2][0] = a[2][1]

  Tao[0][k][r] = exp((-a[0][k])/(T[r]))
  Tao[1][k][r] = exp((-a[1][k])/(T[r]))
  Tao[2][k][r] = exp((-a[2][k])/(T[r]))

  s1[k][r]  = (G1[0]*Tao[0][k][r])+(G1[1]*Tao[1][k][r])+(G1[2]*Tao[2][k][r])
  s2[k][r]  = (G2[0]*Tao[0][k][r])+(G2[1]*Tao[1][k][r])+(G2[2]*Tao[2][k][r])

  eta[k][r]   = (s1[k][r]*X1[r])+(s2[k][r]*X2[r])

  J1[r] = r1/(r1*X1[r]+r2*X2[r])
  J2[r] = r2/(r1*X1[r]+r2*X2[r])
  L1[r] = q1/(q1*X1[r]+q2*X2[r])
  L2[r] = q2/(q1*X1[r]+q2*X2[r])

  lnGammaC1[r] = 1 - J1[r] + ln(J1[r]) - 5*q1*(1 - J1[r]/L1[r] + ln(J1[r]/L1[r]))
  lnGammaC2[r] = 1 - J2[r] + ln(J2[r]) - 5*q2*(1 - J2[r]/L2[r] + ln(J2[r]/L2[r]))

  I1[k][r] = ((Theta[k][r]*s1[k][r]/eta[k][r] - G1[k]*ln(s1[k][r]/eta[k][r])))
```

```
  I2[k][r] = ((Theta[k][r]*s2[k][r]/eta[k][r] - G2[k]*ln(s2[k][r]/eta[k][r])))

  lnGammaR1[r] = q1*(1 - ln(L1[r])) - (I1[0][r]+ I1[1][r]+I1[2][r])
  lnGammaR2[r] = q2*(1 - ln(L2[r])) - (I2[0][r]+ I2[1][r]+I2[2][r])

  LnGammal_1[r]  = lnGammaC1[r] + lnGammaR1[r]
  LnGammal_2[r]  = lnGammaC2[r] + lnGammaR2[r]

  Gamma1[r] = exp(LnGammal_1[r])
  Gamma2[r] = exp(LnGammal_2[r])


#*********************************************************************

0 = ln(X1[r]) + LnGammal_1[r] + (-deltaH1/8.314) *(1/Tm1 - 1/T[r])

#Least Square objective function
res1[r] = T[r]- Texp[r]

Fobj = (sum_r(res1[r])^2))/N


#Maximum likelihood function for a normal distribution
  error[r] = (Texp[r] - T[r])^2
  SSUM     = sum_r(error[r])
  res1[r] = T[r]-Texp[r]
  RSUM     = sum_r((res1[r])^2)

Res_Temp[r] = abs(res1[r]/Texp[r])
Total_Res_Temp = ((sum_r(Res_Temp[r]))*100)/N

Obj_lnf  = -(-0.5*N*ln(2*PI) - N*ln(SIGMA) - SSUM/(2*SIGMA^2) )
```

SLE – FST (Temperature calculation)

```
## New method for SLE Thermodynamic Consistency Test

#Work developed together with Prof. J. O´Connell - University of Virginia

#Larissa P. Cunico 2013

#*********************************************************************


0 = (ln(X1calc[r]))*T[r] - ((DeltaH1)/8.314)*(((1*T[r])/Tm1)-1)+(c*((2*X1calc[r])-
(X1calc[r]^2)))+((a*T[r])+b)


#*********************************************************************

#Least Square objective function

Res1[r] = T[r]- Texp[r]

Fobj = (sum_r(Res1[r])^2))/NN


#Maximum likelihood function for a normal distribution
  error[r] = (Texp[r] - T[r])^2
  SSUM      = sum_r(error[r])
  res1[r] = T[r]-Texp[r]
  RSUM      = sum_r((res1[r])^2)

Res_Temp[r] = abs(res1[r]/Texp[r])
Total_Res_Temp = ((sum_r(Res_Temp[r]))*100)/N

 Obj_lnf  = -(-0.5*N*ln(2*PI) - N*ln(SIGMA) - SSUM/(2*SIGMA^2) )
```

SLE – NRTL Model (Molar Fraction calculation)

```
#NRTL model for liquid phase

# Parameter estimation for NRTL model for binary mixtures and isobaric
# systems and Bubble T calculation
# NRTL model + Ideal Vapour Phase

# CAPEC 2012 Larissa P. Cunico


#**********************************************************************

#Variable and parameters description

# P                                 Pressure [kPa]
# T                                 Temperature [K]
# X                                 Mole fraction of the liquid phase
# Y                                 Mole fraction of the vapour phase

# R                                 Universal gas constant
# Gamma                                 Activity coefficient

# par1=g12-g22 ,  par2=g21-g11 , alpha_1_2          Parameters estimated

#**********************************************************************

# Model equations:

# Calculate interaction terms Tau and G
# par1=g12-g22
# par2=g21-g11
Tau_1_2[r]= par1/(R*T[r])
Tau_2_1[r]= par2/(R*T[r])

G_1_2[r] = exp(-alpha_1_2*Tau_1_2[r])
G_2_1[r] = exp(-alpha_1_2*Tau_2_1[r])

#Calculate Mol fraction 2
X2[r]= 1 - X1[r]
```

```
#Calculate Ln(Gamma)for liquid phase
LnGammal_1[r]= X2[r]^2*Tau_2_1[r]*(G_2_1[r]/(X1[r]+X2[r]*G_2_1[r]))^2 +
X2[r]^2*Tau_1_2[r]*G_1_2[r]/(X2[r]+X1[r]*G_1_2[r])^2
LnGammal_2[r]= X1[r]^2*Tau_1_2[r]*(G_1_2[r]/(X2[r]+X1[r]*G_1_2[r]))^2 +
X1[r]^2*Tau_2_1[r]*G_2_1[r]/(X1[r]+X2[r]*G_2_1[r])^2

Gamma1[r] = exp(LnGammal_1[r])
Gamma2[r] = exp(LnGammal_2[r])

#**********************************************************************

0 = ln(X1[r]) + LnGammal_1[r] + (-deltaH1/8.314) *(1/Tm1 - 1/T[r])



#Least Square objective function
res1[r] = X1[r] - X1exp[r]

Fobj = (sum_r((res1[r])^2))/N

#Maximum likelihood function for a normal distribution
  error[r] = (X1exp[r] - X1[r])^2
  SSUM     = sum_r(error[r])
  res1[r] = X1[r]-X1exp[r]
  RSUM     = sum_r((res1[r])^2)

Res_Xemp[r] = abs(res1[r])
Total_Res_Xemp = ((sum_r(Res_Xemp[r]))*100)/N

Obj_lnf  = -(-0.5*N*ln(2*PI) - N*ln(SIGMA) - SSUM/(2*SIGMA^2) )
```

SLE – UNIQUAC Model (Molar Fraction calculation)

```
# UNIQUAC model for the liquid phase

# Parameter estimation for UNIQUAC model for binary mixtures and
# isobaric systems
# UNIQUAC model

# Capec 2012 Larissa P. Cunico


#**********************************************************************

#Variable and parameters description

# P                     Pressure [kPa]
# T                     Temperature [K]
# X                     Mole fraction of the liquid phase
# Y                     Mole fraction of the vapour phase

# R                     Universal gas constant
# Gamma                     Activity coefficient

# u12_u22 , u21_u11         Parameters estimated for UNIQUAC model
# r, q                          Parameters listed for UNIQUAC model


#**********************************************************************


# For the liquid phase - UNIQUAC model equations:

#Calculate Mol fraction 2
 X2[r] = 1 - X1[r]

#For the calculation of volume parameter (r) and surface area parameter (q)
r1 = sum_k(v1[k]*R[k])
r2 = sum_k(v2[k]*R[k])
q1 = sum_k(v1[k]*Q[k])
q2 = sum_k(v2[k]*Q[k])
```

```
#Calculation of gamma of liquid phase
 Ph1[r] = (r1*X1[r])/(r1*X1[r]+r2*X2[r])
 Ph2[r] = (r2*X2[r])/(r1*X1[r]+r2*X2[r])

 Theta1[r] = (q1*X1[r])/(q1*X1[r]+q2*X2[r])
 Theta2[r] = (q2*X2[r])/(q1*X1[r]+q2*X2[r])

 l1 = 5*(r1-q1)-(r1-1)
 l2 = 5*(r2-q2)-(r2-1)

 Tau12[r] = exp(-u12_u22/(R*T[r]))
 Tau21[r] = exp(-u21_u11/(R*T[r]))


 A1[r]= q1*ln(Theta1[r]+Theta2[r]*Tau21[r])
 A2[r]= q2*ln(Theta2[r]+Theta1[r]*Tau12[r])

 C1[r]=(Tau21[r]/(Theta1[r]+Theta2[r]*Tau21[r]))-(Tau12[r]/(Theta2[r]+Theta1[r]*Tau12[r]))
 C2[r]=(Tau12[r]/(Theta2[r]+Theta1[r]*Tau12[r]))-(Tau21[r]/(Theta1[r]+Theta2[r]*Tau21[r]))


 LnGammal_1[r] = ln(Ph1[r]/X1[r]) + 5*q1*ln(Theta1[r]/Ph1[r])+Ph2[r]*(l1-(l2*(r1/r2)))- A1[r] +
Theta2[r]*q1*C1[r]
 LnGammal_2[r] = ln(Ph2[r]/X2[r]) + 5*q2*ln(Theta2[r]/Ph2[r])+Ph1[r]*(l2-(l1*(r2/r1)))- A2[r] +
Theta1[r]*q2*C2[r]

 Gamma1[r] = exp(LnGammal_1[r])
 Gamma2[r] = exp(LnGammal_2[r])

#*********************************************************************

0 = ln(X1[r]) + LnGammal_1[r] + (-deltaH1/8.314) *(1/Tm1 - 1/T[r])

#Least Square objective function
res1[r] = X1[r] - X1exp[r]

Fobj = (sum_r((res1[r])^2))/N

#Maximum likelihood function for a normal distribution
  error[r] = (X1exp[r] - X1[r])^2
```

```
  SSUM      = sum_r(error[r])
  res1[r] = X1[r]-X1exp[r]
  RSUM      = sum_r((res1[r])^2)

Res_Xemp[r] = abs(res1[r])
Total_Res_Xemp = ((sum_r(Res_Xemp[r]))*100)/N

Obj_lnf  = -(-0.5*N*ln(2*PI) - N*ln(SIGMA) - SSUM/(2*SIGMA^2) )
```

SLE – original UNIFAC Model (Molar Fraction calculation)

```
# UNIFAC model for the liquid phase

# Parameter estimation for UNIFAC model for binary mixtures and isobaric systems
# UNIFAC model

#*Mauricio Sales-Cruz
#*CAPEC, DTU, DK
#*15.02.05

#+ modifications
# Capec 2012 Larissa P. Cunico

#**********************************************************************



#Variable and parameters description

# P                     Pressure [kPa]
# T                     Temperature [K]
# X                     Mole fraction of the liquid phase
# Y                     Mole fraction of the vapour phase

# R                     Universal gas constant
# Gamma                     Activity coefficient
# GammaC                    Activity coefficient combinatorial
# GammaR                    Activity coefficient residual

#v1[k]                          Number of groups of kind k

# r, q                          Pure component volume and are parameters
# Rk, Qk                            Group volume and area parameters
# -a1[n]                        Group binary interaction parameters



#**********************************************************************
# ATTETION the number of the first index of Tao1[0][k][r] (in this case 0) should be changed

#Calculate Mol fraction 2
```

```
 X2[r] = 1 - X1[r]

#Model equations:

  r1 = sum_k(v1[k]*R[k])
  r2 = sum_k(v2[k]*R[k])
  q1 = sum_k(v1[k]*Q[k])
  q2 = sum_k(v2[k]*Q[k])

  G1[k]  = v1[k]*Q[k]
  G2[k]  = v2[k]*Q[k]

  Theta[k][r] = (G1[k]*X1[r])+(G2[k]*X2[r])

# The interaction parameters should not vary in the subgroups
# Set of condition for binary interaction parameters of CH3 (1) and CH2 (2)
  a[0][2] = a[1][2]
  a[2][0] = a[2][1]

  Tao[0][k][r] = exp((-a[0][k])/(T[r]))
  Tao[1][k][r] = exp((-a[1][k])/(T[r]))
  Tao[2][k][r] = exp((-a[2][k])/(T[r]))

  s1[k][r]  = (G1[0]*Tao[0][k][r])+(G1[1]*Tao[1][k][r])+(G1[2]*Tao[2][k][r])
  s2[k][r]  = (G2[0]*Tao[0][k][r])+(G2[1]*Tao[1][k][r])+(G2[2]*Tao[2][k][r])

  eta[k][r]   = (s1[k][r]*X1[r])+(s2[k][r]*X2[r])

  J1[r] = r1/(r1*X1[r]+r2*X2[r])
  J2[r] = r2/(r1*X1[r]+r2*X2[r])
  L1[r] = q1/(q1*X1[r]+q2*X2[r])
  L2[r] = q2/(q1*X1[r]+q2*X2[r])

  lnGammaC1[r] = 1 - J1[r] + ln(J1[r]) - 5*q1*(1 - J1[r]/L1[r] + ln(J1[r]/L1[r]))
  lnGammaC2[r] = 1 - J2[r] + ln(J2[r]) - 5*q2*(1 - J2[r]/L2[r] + ln(J2[r]/L2[r]))

  I1[k][r] = ((Theta[k][r]*s1[k][r]/eta[k][r] - G1[k]*ln(s1[k][r]/eta[k][r])))
  I2[k][r] = ((Theta[k][r]*s2[k][r]/eta[k][r] - G2[k]*ln(s2[k][r]/eta[k][r])))

  lnGammaR1[r] = q1*(1 - ln(L1[r])) - (I1[0][r]+ I1[1][r]+I1[2][r])
```

```
  lnGammaR2[r] = q2*(1 - ln(L2[r])) - (I2[0][r]+ I2[1][r]+I2[2][r])

  LnGammal_1[r]  = lnGammaC1[r] + lnGammaR1[r]
  LnGammal_2[r]  = lnGammaC2[r] + lnGammaR2[r]

  Gamma1[r] = exp(LnGammal_1[r])
  Gamma2[r] = exp(LnGammal_2[r])


#**********************************************************************

0 = ln(X1[r]) + LnGammal_1[r] + (-deltaH1/8.314) *(1/Tm1 - 1/T[r])

#Least Square objective function
res1[r] = X1[r] - X1exp[r]

Fobj = (sum_r((res1[r])^2))/N

#Maximum likelihood function for a normal distribution
  error[r] = (X1exp[r] - X1[r])^2
  SSUM     = sum_r(error[r])
  res1[r] = X1[r]-X1exp[r]
  RSUM     = sum_r((res1[r])^2)

Res_Xemp[r] = abs(res1[r])
Total_Res_Xemp = ((sum_r(Res_Xemp[r]))*100)/N

Obj_lnf  = -(-0.5*N*ln(2*PI) - N*ln(SIGMA) - SSUM/(2*SIGMA^2) )
```

SLE – FST (Molar Fraction calculation)

```
## New method for SLE Thermodynamic Consistency Test

#Work developed together with Prof. J. O´Connell - University of Virginia

#Larissa P. Cunico 2013

#*********************************************************************

f2zero[r] = c/ T[r]
0 = X1calc[r] - exp((DeltaH1/8.314)*((1/Tm1)-(1/T[r]))-(f2zero[r]*((2*X1calc[r])-(X1calc[r]^2)))-
(a+(b/T[r])))


Gamma1exp[r] = exp((DeltaH1/8.314)*((1/Tm1)-(1/T[r])) - ln(X1calc[r]))
Gamma1[r] = exp((f2zero[r]*((2*X1calc[r])-X1calc[r]^2)))+(a+(b/T[r])))


#*********************************************************************

#Least Square Objective function

Res1[r] = X1calc[r]- X1exp[r]

Total_Res_X1 = ((sum_r(Res1[r]))*100)/N

Fobj = (sum_r(Res1[r])^2))/NN

#Maximum likelihood funtion for a normal distribution
  error[r] = (X1exp[r] - X1calc[r])^2
  SSUM     = sum_r(error[r])
  res1[r] = X1calc[r]-X1exp[r]
  RSUM     = sum_r((res1[r])^2)

Res_Xemp[r] = abs(res1[r])
Total_Res_Xemp = ((sum_r(Res_Xemp[r]))*100)/N

 Obj_lnf  = -(-0.5*N*ln(2*PI) - N*ln(SIGMA) - SSUM/(2*SIGMA^2) )
```

LLE by flash calculation – NRTL Model

```
#NRTL model for liquid phase plus LLE calculation

# Parameter estimation for NRTL model for binary mixtures and isobaric
# systems
# NRTL model

# CAPEC 2014 Larissa P. Cunico

#*********************************************************************

#Variable and parameters description

# P                                 Pressure [kPa]
# T                                 Temperature [K]
# X                                 Mole fraction of the liquid phase
# Y                                 Mole fraction of the vapour phase

# R                                 Universal gas constant
# Gamma                                 Activity coefficient

# par1=g12-g22 ,  par2=g21-g11 , alpha_1_2          Parameters estimated

#*********************************************************************


# NRTL Model equations:

# Calculate interaction terms Tau and G
# par1=g12-g22
# par2=g21-g11

#Tau_1_2[r]= par1/(R*T[r])
#Tau_2_1[r]= par2/(R*T[r])
Tau_1_2[r]= a1+b1/T[r]
Tau_2_1[r]= a2+b2/T[r]

G_1_2[r] = exp(-alpha_1_2*Tau_1_2[r])
G_2_1[r] = exp(-alpha_1_2*Tau_2_1[r])
```

```
#Calculate Ln(Gamma)for liquid phase (Phase 1)
LnGammal_1X[r]= X2[r]^2*Tau_2_1[r]*(G_2_1[r]/(X1[r]+X2[r]*G_2_1[r]))^2 +
X2[r]^2*Tau_1_2[r]*G_1_2[r]/(X2[r]+X1[r]*G_1_2[r])^2
LnGammal_2X[r]= X1[r]^2*Tau_1_2[r]*(G_1_2[r]/(X2[r]+X1[r]*G_1_2[r]))^2 +
X1[r]^2*Tau_2_1[r]*G_2_1[r]/(X1[r]+X2[r]*G_2_1[r])^2

Gamma1X[r] = exp(LnGammal_1X[r])
Gamma2X[r] = exp(LnGammal_2X[r])

#Calculate Ln(Gamma)for liquid phase (Phase 2)
LnGammal_1Y[r]= Y2[r]^2*Tau_2_1[r]*(G_2_1[r]/(Y1[r]+Y2[r]*G_2_1[r]))^2 +
Y2[r]^2*Tau_1_2[r]*G_1_2[r]/(Y2[r]+Y1[r]*G_1_2[r])^2
LnGammal_2Y[r]= Y1[r]^2*Tau_1_2[r]*(G_1_2[r]/(Y2[r]+Y1[r]*G_1_2[r]))^2 +
Y1[r]^2*Tau_2_1[r]*G_2_1[r]/(Y1[r]+Y2[r]*G_2_1[r])^2

Gamma1Y[r] = exp(LnGammal_1Y[r])
Gamma2Y[r] = exp(LnGammal_2Y[r])

#----------Liquid liquid equilibrium----------

0 = X1[r]*Gamma1X[r] - Y1[r]*Gamma1Y[r]
0 = X2[r]*Gamma2X[r] - Y2[r]*Gamma2Y[r]

0 = 1 - X1[r] - X2[r]
0 = 1 - Y1[r] - Y2[r]

0 = Z1[r] - X1[r]*taux[r] - Y1[r]*tauy[r]
0 = Z2[r] - X2[r]*taux[r] - Y2[r]*tauy[r]

Fobj[r] = ((Xexp1[r] - X1[r])^2)+((Xexp2[r] - X2[r])^2)+((Yexp1[r] - Y1[r])^2)+((Yexp2[r] - Y2[r])^2)

FFobj = sum_r (Fobj[r])
```

LLE by flash calculation – UNIQUAC Model

```
# UNIQUAC model for the liquid phase

# Parameter estimation for UNIQUAC model for binary mixtures and isobaric systems
# UNIQUAC model

# Capec 2014 Larissa P. Cunico

#*********************************************************************

#Variable and parameters description

# P                     Pressure [kPa]
# T                     Temperature [K]
# X                     Mole fraction of the liquid phase
# Y                     Mole fraction of the vapour phase

# R                     Universal gas constant
# Gamma                 Activity coefficient

# u12_u22 , u21_u11     Parameters estimated for UNIQUAC model
# r, q                  Parameters listed for UNIQUAC model


#*********************************************************************


# For the liquid phase - UNIQUAC model equations:

#For the calculation of volume parameter (r) and surface area parameter (q)
 r1 = sum_k(v1[k]*R[k])
 r2 = sum_k(v2[k]*R[k])
 q1 = sum_k(v1[k]*Q[k])
 q2 = sum_k(v2[k]*Q[k])

#Calculation of gamma of liquid phase
 Ph1X[r] = (r1*X1[r])/(r1*X1[r]+r2*X2[r])
 Ph2X[r] = (r2*X2[r])/(r1*X1[r]+r2*X2[r])

 Ph1Y[r] = (r1*Y1[r])/(r1*Y1[r]+r2*Y2[r])
```

```
Ph2Y[r] = (r2*Y2[r])/(r1*Y1[r]+r2*Y2[r])

Theta1X[r] = (q1*X1[r])/(q1*X1[r]+q2*X2[r])
Theta2X[r] = (q2*X2[r])/(q1*X1[r]+q2*X2[r])

Theta1Y[r] = (q1*Y1[r])/(q1*Y1[r]+q2*Y2[r])
Theta2Y[r] = (q2*Y2[r])/(q1*Y1[r]+q2*Y2[r])

l1 = 5*(r1-q1)-(r1-1)
l2 = 5*(r2-q2)-(r2-1)

#Tau12[r] = exp(-u12_u22/(R*T[r]))
#Tau21[r] = exp(-u21_u11/(R*T[r]))

Tau12[r] = exp(a1+b1/T[r])
Tau21[r] = exp(a2+b2/T[r])

A1X[r]= q1*ln(Theta1X[r]+Theta2X[r]*Tau21[r])
A2X[r]= q2*ln(Theta2X[r]+Theta1X[r]*Tau12[r])

A1Y[r]= q1*ln(Theta1Y[r]+Theta2Y[r]*Tau21[r])
A2Y[r]= q2*ln(Theta2Y[r]+Theta1Y[r]*Tau12[r])

C1X[r]=(Tau21[r]/(Theta1X[r]+Theta2X[r]*Tau21[r]))-(Tau12[r]/(Theta2X[r]+Theta1X[r]*Tau12[r]))
C2X[r]=(Tau12[r]/(Theta2X[r]+Theta1X[r]*Tau12[r]))-(Tau21[r]/(Theta1X[r]+Theta2X[r]*Tau21[r]))


C1Y[r]=(Tau21[r]/(Theta1Y[r]+Theta2Y[r]*Tau21[r]))-(Tau12[r]/(Theta2Y[r]+Theta1Y[r]*Tau12[r]))
C2Y[r]=(Tau12[r]/(Theta2Y[r]+Theta1Y[r]*Tau12[r]))-(Tau21[r]/(Theta1Y[r]+Theta2Y[r]*Tau21[r]))

lnGamma1X[r] = ln(Ph1X[r]/X1[r]) + 5*q1*ln(Theta1X[r]/Ph1X[r])+Ph2X[r]*(l1-(l2*(r1/r2)))- A1X[r]
+ Theta2X[r]*q1*C1X[r]
lnGamma2X[r] = ln(Ph2X[r]/X2[r]) + 5*q2*ln(Theta2X[r]/Ph2X[r])+Ph1X[r]*(l2-(l1*(r2/r1)))- A2X[r]
+ Theta1X[r]*q2*C2X[r]

lnGamma1Y[r] = ln(Ph1Y[r]/Y1[r]) + 5*q1*ln(Theta1Y[r]/Ph1Y[r])+Ph2Y[r]*(l1-(l2*(r1/r2)))- A1Y[r]
+ Theta2Y[r]*q1*C1Y[r]
lnGamma2Y[r] = ln(Ph2Y[r]/Y2[r]) + 5*q2*ln(Theta2Y[r]/Ph2Y[r])+Ph1Y[r]*(l2-(l1*(r2/r1)))- A2Y[r]
+ Theta1Y[r]*q2*C2Y[r]
```

```
Gamma1X[r] = exp(lnGamma1X[r])
Gamma2X[r] = exp(lnGamma2X[r])

Gamma1Y[r] = exp(lnGamma1Y[r])
Gamma2Y[r] = exp(lnGamma2Y[r])


#----------------------Liquid liquid equilibrium----------------------

0 = X1[r]*Gamma1X[r] - Y1[r]*Gamma1Y[r]
0 = X2[r]*Gamma2X[r] - Y2[r]*Gamma2Y[r]

0 = 1 - X1[r] - X2[r]
0 = 1 - Y1[r] - Y2[r]

0 = Z1[r] - X1[r]*taux[r] - Y1[r]*tauy[r]
0 = Z2[r] - X2[r]*taux[r] - Y2[r]*tauy[r]

Fobj[r] = ((Xexp1[r] - X1[r])^2)+((Xexp2[r] - X2[r])^2)+((Yexp1[r] - Y1[r])^2)+((Yexp2[r] - Y2[r])^2)

FFobj = sum_r (Fobj[r])
```

LLE by flash calculation – Original UNIFAC Model

```
# Code for the regression of UNIFAC binary parameters
# based on experimental LLE data

# Work based on "Mauricio Sales-Cruz, 2005"
# and "Larissa P. Cunico, 2013"

# Further modified by Michele Mattei, 2013
# and Larissa P. Cunico, 2014

#*********************************************************************

# Variable and parameters description

# Must be defined under "Define Relationship"

# k                    Number of UNIFAC group involved

# Must be defined under "Set Variable Value", for each experimental data "r"

# T          Temperature [K]
# X1E            Mole fraction of the component 1 in the first liquid # phase
# Y1E                Mole fraction of the component 1 in the second
# liquid phase

# Must be defined under "Set Variable Value" for each UNIFAC group "k"

# R[k], Q[k}       UNIFAC group volume and area parameters
# v1[k]              Number of UNIFAC groups "k" for the component 1
# v2[k]              Number of UNIFAC groups "k" for the component 2
# -a[n][k]           UNIFAC group binary interaction parameters between
# groups "n" and "k"

#*********************************************************************

# UNIFAC model equations

  r1 = sum_k(v1[k]*R[k])
  r2 = sum_k(v2[k]*R[k])
```

```
q1 = sum_k(v1[k]*Q[k])
q2 = sum_k(v2[k]*Q[k])

G1[k]  = v1[k]*Q[k]
G2[k]  = v2[k]*Q[k]

# Set of condition for binary interaction parameters of CH3 (1) and CH2 (2)
a[1][3] = a[2][3]
a[1][4] = a[2][4]
a[3][1] = a[3][2]
a[4][1] = a[4][2]

ThetaX[1][r] = (G1[1]*X1[r])+(G2[1]*X2[r])
ThetaX[2][r] = (G1[2]*X1[r])+(G2[2]*X2[r])
ThetaX[3][r] = (G1[3]*X1[r])+(G2[3]*X2[r])
ThetaX[4][r] = (G1[4]*X1[r])+(G2[4]*X2[r])

ThetaY[1][r] = (G1[1]*Y1[r])+(G2[1]*Y2[r])
ThetaY[2][r] = (G1[2]*Y1[r])+(G2[2]*Y2[r])
ThetaY[3][r] = (G1[3]*Y1[r])+(G2[3]*Y2[r])
ThetaY[4][r] = (G1[4]*Y1[r])+(G2[4]*Y2[r])

Tao[1][k][r] = exp((-a[1][k])/(T[r]))
Tao[2][k][r] = exp((-a[2][k])/(T[r]))
Tao[3][k][r] = exp((-a[3][k])/(T[r]))
Tao[4][k][r] = exp((-a[4][k])/(T[r]))

s1[k][r]  = (G1[1]*Tao[1][k][r])+(G1[2]*Tao[2][k][r])+(G1[3]*Tao[3][k][r])+(G1[4]*Tao[4][k][r])
s2[k][r]  = (G2[1]*Tao[1][k][r])+(G2[2]*Tao[2][k][r])+(G2[3]*Tao[3][k][r])+(G2[4]*Tao[4][k][r])

etaX[1][r]   = (s1[1][r]*X1[r])+(s2[1][r]*X2[r])
etaX[2][r]   = (s1[2][r]*X1[r])+(s2[2][r]*X2[r])
etaX[3][r]   = (s1[3][r]*X1[r])+(s2[3][r]*X2[r])
etaX[4][r]   = (s1[4][r]*X1[r])+(s2[4][r]*X2[r])

etaY[1][r]   = (s1[1][r]*Y1[r])+(s2[1][r]*Y2[r])
etaY[2][r]   = (s1[2][r]*Y1[r])+(s2[2][r]*Y2[r])
etaY[3][r]   = (s1[3][r]*Y1[r])+(s2[3][r]*Y2[r])
etaY[4][r]   = (s1[4][r]*Y1[r])+(s2[4][r]*Y2[r])
```

```
J1X[r] = r1/(r1*X1[r]+r2*X2[r])
J2X[r] = r2/(r1*X1[r]+r2*X2[r])
L1X[r] = q1/(q1*X1[r]+q2*X2[r])
L2X[r] = q2/(q1*X1[r]+q2*X2[r])

J1Y[r] = r1/(r1*Y1[r]+r2*Y2[r])
J2Y[r] = r2/(r1*Y1[r]+r2*Y2[r])
L1Y[r] = q1/(q1*Y1[r]+q2*Y2[r])
L2Y[r] = q2/(q1*Y1[r]+q2*Y2[r])

lnGammaC1X[r] = 1 - J1X[r] + ln(J1X[r]) - 5*q1*(1 - J1X[r]/L1X[r] + ln(J1X[r]/L1X[r]))
lnGammaC2X[r] = 1 - J2X[r] + ln(J2X[r]) - 5*q2*(1 - J2X[r]/L2X[r] + ln(J2X[r]/L2X[r]))

lnGammaC1Y[r] = 1 - J1Y[r] + ln(J1Y[r]) - 5*q1*(1 - J1Y[r]/L1Y[r] + ln(J1Y[r]/L1Y[r]))
lnGammaC2Y[r] = 1 - J2Y[r] + ln(J2Y[r]) - 5*q2*(1 - J2Y[r]/L2Y[r] + ln(J2Y[r]/L2Y[r]))

I1X[k][r] = ((ThetaX[k][r]*s1[k][r]/etaX[k][r] - G1[k]*ln(s1[k][r]/etaX[k][r])))
I2X[k][r] = ((ThetaX[k][r]*s2[k][r]/etaX[k][r] - G2[k]*ln(s2[k][r]/etaX[k][r])))

I1Y[k][r] = ((ThetaY[k][r]*s1[k][r]/etaY[k][r] - G1[k]*ln(s1[k][r]/etaY[k][r])))
I2Y[k][r] = ((ThetaY[k][r]*s2[k][r]/etaY[k][r] - G2[k]*ln(s2[k][r]/etaY[k][r])))

lnGammaR1X[r] = q1*(1 - ln(L1X[r])) - (I1X[1][r]+I1X[2][r]+I1X[3][r]+I1X[4][r])
lnGammaR2X[r] = q2*(1 - ln(L2X[r])) - (I2X[1][r]+I2X[2][r]+I2X[3][r]+I2X[4][r])

lnGammaR1Y[r] = q1*(1 - ln(L1Y[r])) - (I1Y[1][r]+I1Y[2][r]+I1Y[3][r]+I1Y[4][r])
lnGammaR2Y[r] = q2*(1 - ln(L2Y[r])) - (I2Y[1][r]+I2Y[2][r]+I2Y[3][r]+I2Y[4][r])

lnGamma1X[r]  = lnGammaC1X[r] + lnGammaR1X[r]

lnGamma2X[r]  = lnGammaC2X[r] + lnGammaR2X[r]

lnGamma1Y[r]  = lnGammaC1Y[r] + lnGammaR1Y[r]
lnGamma2Y[r]  = lnGammaC2Y[r] + lnGammaR2Y[r]

Gamma1X[r] = exp(lnGamma1X[r])
Gamma2X[r] = exp(lnGamma2X[r])

Gamma1Y[r] = exp(lnGamma1Y[r])
Gamma2Y[r] = exp(lnGamma2Y[r])
```

#----------Liquid liquid equilibrium----------

0 = X1[r]*Gamma1X[r] - Y1[r]*Gamma1Y[r]

0 = X2[r]*Gamma2X[r] - Y2[r]*Gamma2Y[r]

0 = 1 - X1[r] - X2[r]

0 = 1 - Y1[r] - Y2[r]

0 = Z1[r] - X1[r]*taux[r] - Y1[r]*tauy[r]

0 = Z2[r] - X2[r]*taux[r] - Y2[r]*tauy[r]

Fobj[r] = ((Xexp1[r] - X1[r])^2)+((Xexp2[r] - X2[r])^2)+((Yexp1[r] - Y1[r])^2)+((Yexp2[r] - Y2[r])^2)

FFobj = sum_r (Fobj[r])

Appendix 4

Table 1: Quality factor for VLE data and lipids systems

BINARY MIXTURE		Isob. P (kPa)	Q Factor	TESTS				
LIPID	Second compound			Herington	Van Ness	Point	Inf. Dilution	Endpoint
Lauric acid	Myristic acid	0.533	0.15	Failed	Failed	N/A	Failed	0.51
Lauric acid	Myristic acid	0.53	0.24	Passed	Failed	N/A	Failed	0.42
Lauric acid	Myristic acid	0.5	0.022	Failed	Failed	N/A	Failed	0.13
		6.7	0.35	Failed	Failed	N/A	Failed	1
Lauric acid	Myristic acid	1.3	0.11	Failed	Failed	N/A	Failed	0.32
		0.4	0.0034	Failed	Failed	N/A	Failed	0.028
		6.7	0.12	Failed	Failed	N/A	Failed	0.42
Myristic acid	Palmitic acid	1.3	0.086	Failed	Failed	N/A	Failed	0.26
		0.4	0.11	Failed	Failed	N/A	Failed	0.23
Myristic acid	Palmitic acid	0.5	0.014	Failed	Failed	N/A	Failed	0.095
Myristic acid	Palmitic acid	6.6	0.17	Failed	Failed	N/A	Failed	0.46
Myristic acid	Stearic acid	6.6	0.13	Passed	Failed	N/A	Failed	0.21
Palmitic acid	Stearic acid	6.6	0.052	Failed	Failed	N/A	Failed	0.17
Palmitic acid	Stearic acid	0.5	0.25	N/A	N/A	N/A	N/A	N/A

Table 1: Quality factor for VLE data and lipids systems **(Continuation)**

Palmitic acid	Stearic acid	0.67	0.027	Failed	Failed	N/A	Failed	0.15
Oleic acid	Palmitic acid	0.33	0.0068	Failed	Failed	N/A	Failed	0.063
Oleic acid	Palmitic acid	0.67	0.043	Failed	Failed	N/A	Failed	0.29
Methyl Laurate	Methanol	101.3	0.25	N/A	N/A	N/A	N/A	0.5
Methyl Laurate	Ethanol	101.3	0.25	N/A	N/A	N/A	N/A	0.5
Methyl Laurate	Methyl Myristate	13.33	0.25	N/A	N/A	N/A	N/A	N/A
		6.6	0.32	Passed	Failed	N/A	Failed	0.54
		5.3	0.52	Passed	Failed	N/A	Failed	0.8
		4	0.25	N/A	N/A	N/A	N/A	N/A
Methyl Laurate	Lauric acid	0.533	0.027	Failed	Failed	N/A	Failed	0.11
Methyl Myristate	Methanol	101.3	0.25	N/A	N/A	N/A	N/A	0.5
Methyl Myristate	Ethanol	101.3	0.25	N/A	N/A	N/A	N/A	0.5
Methyl myristate	Methyl pamitate	3.9997	0.13	N/A	N/A	N/A	N/A	0.25
Methyl myristate	Methyl pamitate	5.33	0.4	Failed	Passed	N/A	Failed	1
Methyl palmitate	Methyl stearate	0.533	0.024	Failed	Failed	N/A	Failed	0.13
Methyl palmitate	Methyl linoleate	4	0.27	Failed	Failed	N/A	Failed	0.81
Methyl Oleate	Methanol	90	0.25	N/A	N/A	N/A	N/A	N/A
Methyl Oleate	Methanol	70	0.25	N/A	N/A	N/A	N/A	N/A
Methyl Oleate	Methanol	50	0.25	N/A	N/A	N/A	N/A	N/A

Table 1: Quality factor for VLE data and lipids systems **(Continuation)**

Methyl Oleate	Methanol	30	0.25	N/A	N/A	N/A	N/A	N/A
Methyl Oleate	Methanol	101.3	0.25	N/A	N/A	N/A	N/A	0.5
Methyl Oleate	Ethanol	101.3	0.25	N/A	N/A	N/A	N/A	0.5
Ethyl palmitate	Ethyl stearate	5.3329	0.074	Failed	Failed	N/A	Failed	0.3
Ethyl Palmitate	Ethyl oleate	5.3329	0.097	Passed	Failed	N/A	Failed	0.14
Ethyl Palmitate	Ethyl oleate							
Ethyl linoleate	Ethyl Palmitate	9.3326	0.024	Failed	Failed	N/A	Failed	0.1
Glycerol	Water	101	0.25	N/A	N/A	N/A	N/A	0.35
Glycerol	Water	101.325	0.079	Passed	Failed	N/A	Failed	0.18
		95.3	1	N/A	Passed	N/A	N/A	1
		63.84	0.62	Failed	Passed	N/A	Passed	0.89
Glycerol	Water	54.72	0.53	Failed	Passed	N/A	Failed	0.84
		41.54	0.49	Failed	Passed	N/A	Failed	0.75
		29.38	0.47	Passed	Passed	N/A	Failed	0.62
		14.19	0.36	Passed	Passed	N/A	Failed	0.51
Glycerol	Ethanol	101.3	-	-	-	-	-	-

Table 1: Quality factor for VLE data and lipids systems **(Continuation)**

		66.7	0.33	N/A	N/A	N/A	N/A	0.67
		60	0.33	N/A	N/A	N/A	N/A	0.67
		53.3	0.33	N/A	N/A	N/A	N/A	0.67
		46.7	0.07	N/A	N/A	N/A	N/A	0.14
Ethanol	Glycerol	40	0.33	N/A	N/A	N/A	N/A	0.67
		33.3	0.15	N/A	N/A	N/A	N/A	0.31
		20	-	-	-	-	-	-
		13.3	0.21	N/A	N/A	N/A	N/A	0.41
		6.7	0.17	N/A	N/A	N/A	N/A	0.35
		101.3	0.25	N/A	N/A	N/A	N/A	0.5
		90	0.25	N/A	N/A	N/A	N/A	0.5
Glycerol	Methanol	70	0.25	N/A	N/A	N/A	N/A	0.5
		50	0.25	N/A	N/A	N/A	N/A	0.5
		30	0.25	N/A	N/A	N/A	N/A	0.5
Glycerol	Methanol	101	0.25	N/A	N/A	N/A	N/A	0.5
Glycerol	Methanol	32.02	0.33	N/A	N/A	N/A	N/A	0.65
		45.3	0.38	N/A	N/A	N/A	N/A	0.75
Methanol	Glycerol	66.7	0.33	N/A	N/A	N/A	N/A	0.67

Table 2: Quality factor for SLE data and lipids systems

BINARY MIXTURE		TESTS			
LIPID	Second compound	Final	Endpoint	Van Ness	FST
Lauric Acid	Myristic acid	0.583	0.241	0.773	0.735
Lauric Acid	Myristic acid	0.365	0.012	0.149	0.9347
Lauric Acid	Myristic acid	0.926	1.000	0.861	0.9158
Lauric Acid	Myristic acid	0.773	0.649	0.824	0.845
Lauric Acid	Palmitic acid	0.890	1.000	0.857	0.814
Lauric Acid	Stearic Acid	0.595	0.094	0.822	0.869
Lauric Acid	Stearic acid	0.891	1.000	0.822	0.851
Lauric Acid	Stearic acid	0.631	0.254	0.765	0.874
Myristic acid	Palmitic acid	0.656	0.369	0.800	0.799
Myristic acid	Palmitic acid	0.852	0.775	0.897	0.885
Myristic acid	Stearic acid	0.917	0.920	0.917	0.915
Myristic acid	Stearic acid	0.628	0.217	0.797	0.871
Palmitic acid	Stearic acid	0.777	1.000	0.656	0.674
Palmitic acid	Linoleic acid	0.539	N/A	0.405	0.674
Oleic acid	Stearic acid	0.928	1.000	0.855	0.925
Stearic acid	Acetone	0.891	N/A	0.855	0.926

Table 2: Quality factor for SLE data and lipids systems **(Continuation)**

Linoleic acid	Oleic acid	0.906	N/A	0.864	0.948
Oleic acid	Palmitic acid	0.863	N/A	0.780	0.946
POP	PPP	0.158	N/A	0.139	0.176
Triolein	Tripalmitin	0.613	0.006	0.898	0.937
Triolein	Tripalmitin	0.9390	N/A	0.938	0.940
Oleic acid	Tripalmitin	0.666	0.112	0.940	0.946
Oleic acid	Tripalmitin	0.928	N/A	0.914	0.943
Oleic acid	Tripalmitin	0.922	N/A	0.892	0.953
Linoleic	Tripalmitin	0.467	N/A	0.670	0.722
Triolein	Palmitic acid	0.466	0.005	0.670	0.722
Triolein	Palmitic acid	0.653	N/A	0.603	0.703
Triolein	Palmitic acid	0.475	0.005	0.708	0.711
M-Laurate	M-Stearate	0.476	0.061	0.509	0.859
M-Myristate	M-Palmitate	0.654	0.290	0.821	0.851
M-Palmitate	M-Stearate	0.416	0.069	0.395	0.784
M-Palmitate	M-Stearate	0.585	0.179	0.754	0.824
M-Myristate	M-Stearate	0.631	0.200	0.810	0.883
M-Oleate	M-Stearate	0.514	0.117	0.467	0.958
M-Linoleate	M-Stearate	0.463	0.029	0.472	0.888

Table 2: Quality factor for SLE data and lipids systems (Continuation)

E-Laurate	E-Palmitate	0.423	0.040	0.394	0.835
E-Myristate	E-Palmitate	0.449	0.107	0.337	0.902
E-Myristate	E-Stearate	0.590	0.285	0.625	0.861
E-Palmitate	E-Oleate	0.401	0.007	0.351	0.845
E-Laurate	E-Stearate	0.527	0.052	0.651	0.878
E-Linoleate	E-Stearate	0.519	0.003	0.637	0.918
E-Palmitate	E-Linoleate	0.373	0.003	0.217	0.899

Appendix 5

Peer-reviewed publications

• CUNICO, L. P.; HUKKERIKAR, A. S.; CERIANI, R.; SARUP, B.; GANI R. Molecular Structure-Based Methods of Property Prediction in Application to Lipids: A Review and Refinement. Fluid Phase Equilibr, v. 15, p. 2-18, 2013 .

• CUNICO, L. P.; CERIANI, R.; SARUP, B.; O´CONNELL, J. P.; GANI, R. Data, analysis and modelling of physical properties for process design of systems involving lipids. Fluid Phase Equilibr, v. 362, p. 318-327, 2014.

• CUNICO, L. P.; DAMASCENO, D. S.; FALLEIRO, R. M. M. ; SARUP, B. ; ABILDSKOV, J. ; CERIANI, R. ; GANI R. Vapour liquid equilibria of monocaprylin plus palmitic acid or methyl stearate at 1.2 and 2.5 kPa by using DSC Technique. AIChE J. (submitted).

• CUNICO, L. P.; TULA A. K.; CERIANI, R.; GANI R. Modelling and Prediction of Solid Solubility, Wiley – Book chapter (submitted).

Conference and meeting participations

• Invited lecture (Prof. R. Gani) at the 6th International Symposium on Molecular Thermodynamics and Molecular Simulation – Hiroshima – Japan – September 25-28, 2012.

• Oral presentation at the 26th European Symposium on applied Thermodynamics together with Annual Meeting of ProcessNet and VDI GEU Working Parties on Thermodynamics (ESAT 2012) – Potsdam – Germany – October 07-10, 2012.

• Poster at the 9th European Congress of Chemical Engineering (ECCE-09) – The Hague – Netherlands – April 21-25, 2013.

• Poster at the 13th International Conference on Properties and Phase Equilibria for Products and Process Design (PPEPPD 2013) – Iguazu Falls - Argentina / Brazil – May 26-30, 2013.

• Oral presentation at the Capec-Process Annual Meeting 2013 – Snekkersten – Denmark – June 5-7, 2013.

• Oral presentation at the Capec-Process Annual Meeting 2014 – Bella Sky Comwell Hotel Copenhagen – Denmark – June 10-12, 2014.

• Oral presentation (2) at the 27th European Symposium on applied Thermodynamics (ESAT) – Eindhoven University of Technology – The Netherlands – July 6-9, 2014.

• Oral presentation at the 21st International Congress of Chemical and Process Engineering (CHISA) – Prague - Czech Republic – August 23-27, 2014.

• Oral presentation at the AIChE Annual Meeting – Atlanta – USA – November 16-21, 2014.

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